

DIELECTRIC DISPERSION  
IN  
DILUTE CELLULOSE ACETATE SOLUTIONS

by

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Thesis Submitted to the Faculty of the

Virginia Polytechnic Institute

in candidacy for the degree of

Doctor of Philosophy

in

Chemistry

September, 1959

Blacksburg, Virginia

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INTRODUCTION

Previous investigations have revealed that some polymer solutions exhibit dielectric dispersion (variation of the dielectric constant with frequency) which is apparently related in some way to the molecular weight of the polymer. One of the more promising of these investigations was carried out on solutions of cellulose acetate in dioxane. The change in dielectric constant was so small and the frequency range over which the change occurred was so wide, however, that rather concentrated solutions had to be used in order to obtain reproducible results. This was undesirable because of the strong possibility of intermolecular interactions interfering with the measurement and giving rise to spurious results. Such measurements on dilute solutions thus were chosen as the object of the present investigation.

The fundamental difficulty could be attributed to the fact that the change in dielectric constant of a solution containing less than about 1% cellulose acetate was such that the change in a 250-uuf capacitor was only about 0.5 uuf, or less, in a frequency range of three decades. The course of such a small change is difficult to detect over such a wide band of frequencies. Capacitance bridges were available and are very good for making measurements at a single frequency, particularly in the range of frequencies under investigation; but they have certain undesirable characteristics, which make the coverage of such a wide band of frequencies with the necessary



precision rather difficult. The use of ordinary resonance methods would be very desirable, but they are limited by the practical size of the components available to frequencies well above the lowest frequencies which were expected to be encountered. As a result of these limitations, a modified resonance procedure was adopted. A resistance-capacitance controlled oscillator was substituted for the more conventional inductance-capacitance circuits. Null indications were obtained by substituting a frequency counting system of very great precision for the "zero beat" method.

In the earlier work it was found that the critical frequency was related to the weight average molecular weight of the polymer sample, the critical frequency being defined as the frequency at which the dispersion was 0.5. Based on this, it seemed reasonable to assume that the dielectric dispersion curve might be related in some way to the molecular weight distribution curve in the case of a polydisperse sample. All of the measurements were thus designed to give the dielectric dispersion curve in as much detail as possible, since this served the two-fold purpose of permitting conclusions to be drawn concerning the validity of the molecular weight relationship in dilute solutions and giving an indication of any influence of the molecular weight distribution on the dielectric dispersion.

It can be seen that the investigation consisted of two major phases. The first was to devise a method of measurement capable of the precision necessary to determine the dielectric dispersion

curve in sufficient detail to allow conclusions to be drawn, while the second phase consisted of the application of the apparatus to actual measurements and the interpretation of the results obtained. Although the two phases are obviously interrelated, an attempt will be made to keep them separate in the hope that this will tend to clarify the discussion.

The "Literature Review" has been written with the object of providing some of the specialized background information necessary for an understanding of the rest of the thesis. No attempt has been made to provide a comprehensive study of the information available on any phase of the work. Where there was any choice in the matter, the references cited are those which were felt to be of fundamental importance or which are accompanied by extensive bibliographies. An attempt has been made in the "Experimental" section to cover in considerable detail the operation and experimental procedure using the apparatus in its final state of development. Consequently, the course of the development of the apparatus and the details of such routine operations as the determination of intrinsic viscosities have been omitted entirely in an attempt to limit the section to a reasonable length. Although the development and construction of measuring apparatus was a necessary adjunct of the investigation, it was of less importance than the measurements themselves; therefore, the part of the "Discussion of Results" which deals with the apparatus has been limited in length and scope.

LITERATURE REVIEW

## THE ELECTRICAL PROPERTIES OF PHYSICAL MEDIA

In order to avoid ambiguity, it seems advisable to define and discuss briefly some of the electrical terms which will be used extensively. Any physical medium can be described electrically by the three quantities; conductivity,  $\rho$ , permeability,  $\mu$ , and the permittivity,  $\epsilon$ . These three properties of physical media can in turn be regarded as proportionality constants of one kind or another. The permeability and conductivity are of minor importance in this work, so they need not be considered further.

Dielectric Permittivity and Dielectric Constant. The permittivity is of major importance in this discussion, so it will be considered in some detail. The reason that it is important is that it is directly related to the quantity known as the dielectric constant. The fundamental origin of the permittivity is in Coulomb's law, where it arises as the proportionality constant. It can be defined as the ratio of the product of the magnitudes of two charges to the product of the attractive force between the charges and the square of the distance separating them. It may or may not be dimensionless, depending upon the system of units which are chosen and the way in which other quantities in the equation are defined. In the electrostatic system, the constant is dimensionless and in free space equals unity; however, it is neither dimensionless nor equal to unity in free space in the electromagnetic system. Fortunately, the quantity with which we are

concerned is more aptly described as the relative permittivity and, for a given medium, is the ratio of the permittivity of that medium to the permittivity of free space. Dependence upon any particular set of units is thus removed. This ratio is generally referred to in the chemical literature as the dielectric constant and the use of the term dielectric constant in this thesis will mean the relative permittivity. These concepts are fully discussed in basic texts on electricity and magnetism, that of Sears (77) being a typical example. A very fundamental discussion of this aspect of the molecular theory of dielectric properties is given by Jansen (47).

Relation of the Dielectric Constant to Capacitance. The dielectric constant is fairly easily measured as a result of the dependence of the capacitance of any given capacitor on the dielectric constant of the medium between the plates. This dependence arises from the definition of capacitance as the proportionality constant between the charge and voltage of a capacitor. This means that capacitance equals the ratio of the charge stored on the plates to the voltage between the plates. The voltage between the plates depends on the field intensity between the plates and the field intensity in turn is defined by the force exerted on a unit positive test charge placed between the plates. It can thus be seen that since the force is inversely proportional to the dielectric constant, the field intensity will also be inversely proportional to it, and the capacitance will be directly proportional to it.

Dependence of the Dielectric Constant on Molecular Structure. The dielectric constant of matter is greater than that of free space due to

the inherent polarizability of all matter. This can be attributed to a distortion of the charge distribution in the dielectric material in such a way that the centers of positive and negative charge do not coincide. Thus, local fields are set up which reduce the over-all field intensity within the medium. Consequently, according to the definition of the field intensity and the dielectric constant, the dielectric constant must be greater than it is in free space. Thus, the dielectric constant is a function of the extent of the alteration of the configuration and orientation of the molecules of a substance, to give rise to induced fields, when acted upon by an external field.

Frequency Dependence of the Dielectric Constant. There was nothing in the classical field theory to indicate that the dielectric constant should be frequency dependent. However, Cole (11) and Drude (20) found that the dielectric constants of some liquids appeared to vary with frequency in certain frequency and temperature ranges. This variation is always one of decreasing dielectric constant with increasing frequency and is often called anomalous dispersion. It is never found in free space. Following Drude, anomalous dispersion was observed by several authors on substances which are now recognized as polar; for example, Nicholls and Tear (60) and Tear (87).

Debye's Explanation of Anomalous Dispersion. Anomalous dispersion and related problems are treated by Debye in a series of papers beginning in 1912 with the introduction of the concept of a permanent electric moment in the molecule (18) and culminating in 1929 with the publication of the comprehensive monograph, Polar Molecules, (16). In this

treatment it is assumed that anomalous dispersion can be attributed to relaxation phenomena which arises as a result of permanent polarization of the molecules. Relaxation is defined as "the lag in the response of a system to change in the forces to which it is subjected" (48).

This can be explained in the following manner. There is a tendency for the molecules of a substance composed of polar molecules to become oriented in a static electric field. If the impressed field could be removed instantaneously, an appreciable interval of time would be required for the molecules to regain a random orientation. (Since the orientation of polar molecules represents polarization, the term polarization can be adopted.) The decay of polarization is exponential in nature, and theoretically the attainment of a completely random orientation or zero polarization would require an infinite period of time. For this and other reasons the relaxation time,  $\tau$ , is defined as the time required for the polarization of a material to decrease to  $1/e$  of its original value after the instantaneous removal of a static field.

The existence of this dielectric relaxation phenomena means that when the material is placed in a time varying field, the polarization will lag behind the applied field no matter how slow the rate of change of the applied field. If the applied field is sinusoidal, the variation in polarization will be sinusoidal and will lag the applied field in phase. For an applied field having a period very much greater than the relaxation time, the effect of this lag is very small. In the case of an applied field having a period which is about the same order of magnitude as the relaxation time, however, the effect of the lagging

polarization becomes quite noticeable, because the field intensity inside the medium is no longer reduced to the extent that it was in the case of the static field. As a consequence of the definitions of field intensity and dielectric constant, the dielectric constant of the material must be considered to have decreased. This is admittedly a very simplified explanation, because it ignores, among other things, the complication due to thermal movement of the molecules, but it seems adequate for the present purposes.

In his mathematical treatment Debye applied the theory of Brownian movement as developed by Einstein to obtain a general distribution function for the orientation of the molecules in a time varying field (17). The theory predicts both dielectric dispersion and loss which are represented by the real and imaginary components of a complex dielectric constant.

The equations are:

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + X^2} \quad (1)$$

and

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_{\infty}) X}{1 + X^2} \quad (2)$$

where

$$X = \frac{\epsilon_0 + 2}{\epsilon_{\infty} + 2} \omega \tau. \quad (3)$$

In these equations  $\epsilon'$  is described as the real component and  $\epsilon''$  as the imaginary component of the complex dielectric constant. The dielectric constant at zero frequency is  $\epsilon_0$ ; the dielectric constant at infinite frequency is  $\epsilon_\infty$ . Omega is the angular frequency given by:

$$\omega = 2 \pi f \quad (4)$$

where  $f$  is the frequency in cycles per second, c. (The abbreviations for cycles per second and kilocycles per second will be shortened to c and kc in this thesis.)

A quite different approach to the problem was used by Frohlich, but he obtained practically the same equations that Debye obtained (26). The only difference is that in Frohlich's results,  $x$  in equation (3) was given by  $\omega\tau$ . Smyth obtained an expression exactly the same as that of Frohlich by a very similar procedure and attributes the difference between it and Debye's to the fact that Debye considered a molecular relaxation process while Frohlich considered a macroscopic process (79).

The  $\epsilon_0$  and  $\epsilon_\infty$  were defined for the purposes of the derivations as the dielectric constant at zero frequency and infinite frequency respectively, because only one dispersion region (one relaxation time) was assumed in the derivation. In practice this is never true; there is always a multiplicity of relaxation times, because of the different forms of polarization present. The best approach to a single relaxation time which can be attained is the situation where the relaxation times differ greatly and the corresponding dispersion regions do not overlap. In such a case,  $\epsilon_0$  is taken as the value of the dielectric constant at



frequencies below the dispersion region in question and  $\epsilon_{\infty}$  is taken as the value at frequencies above the dispersion region.

In practice, the equation showing the frequency dependence of  $\epsilon$  is usually modified somewhat and a quantity,  $D$ ; which varies from a value of one at the low frequency and to zero at the high frequency end, is used in plots of dispersion. The quantity,  $D$ , is frequently called dispersion, and this terminology will be used in this thesis.

By a simple modification of equation (1) and substitution of (3) we obtain:

$$\frac{\epsilon - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = \frac{1}{1 + \omega^2 \tau^2} \quad (5)$$

where it had been assumed

$$\frac{\epsilon_0 + 2}{\epsilon_{\infty} + 2} \cong 1 \quad (6)$$

which is usually valid. If the measured capacitances at the various frequencies are indicated in the same way that the dielectric constants were, we obtain:

$$\frac{C - C_{\infty}}{C_0 - C_{\infty}} = \frac{\epsilon - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = D \quad (7)$$

because

$$\frac{\frac{C}{C'} - \frac{C_{\infty}}{C'}}{\frac{C_0}{C'} - \frac{C_{\infty}}{C'}} = \frac{\epsilon - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} \quad (8)$$

where  $C'$  is the air capacitance of the dielectric cell.

The advantage of using  $D$  is now obvious. It can be calculated as a function of frequency from a knowledge of the difference between the capacitances of the cell at  $f_0$  and  $f_\infty$  and the difference between the capacitances of the cell at  $f$  and  $f_\infty$ . (The subscripts have the same connotation that they had when used with  $\epsilon$  and  $C$  above.) Thus, the mechanical procedure and the calculations are simplified very much by the use of  $D$ .

It is assumed during the course of these derivations that there is a single relaxation time; that is, that the resistance to rotation is the same for all of the molecules comprising the medium in question. Experiments in which the dielectric behavior of certain substances has been studied show that in some cases, these and other assumptions in the derivation are justified. An excellent example is found in the investigation of *i*-butyl bromide by Hennely, Heston, and Smyth (41). The agreement with the theoretical curves is good. The same investigation showed, however, that *n*-octyl bromide exhibited dielectric dispersion and loss over a much wider band of frequencies than predicted by theory. This was accompanied by a very noticeable decrease in the slope of the dispersion curve at the critical frequency. This behavior is attributed to a multiplicity of relaxation times at such close intervals that the dispersion regions overlap.

It appears to the author that the most important of Debye's assumptions, other than a single relaxation time, was that of neglecting intermolecular interactions. This limits the conditions under which the Debye equation should hold to vapors and dilute solutions of polar

molecules in nonpolar solvents. The effect of the dipoles on each other is usually negligible under such conditions. A great deal of work has been done to obtain an equation which would describe a system of dipoles more accurately in the liquid state. Such an equation would permit calculation of the dipole moments of molecules from measurements of the static dielectric constants of the liquids. Onsager (62) and Kirkwood (49) have had notable success in this direction. Their equations are complicated, however, and so far have not been successfully applied to the problem of anomalous dispersion.

Another assumption which appears to be important, but is not held to be so, is that of a spherical molecule. In the light of some experimental results; those for *i*-butyl bromide and *n*-octyl bromide for example (41); this assumption seems to take on considerable importance, but work done on proteins by Wyman (94) tends to indicate that it is not. It is believed that in the case of the alkyl bromides, the important difference between the two molecules is in the rigidity rather than the shape. The *n*-octyl bromide would be expected to exhibit considerable flexibility in the carbon chain and thus to have a continuum of relaxation times, rather than a series of widely spaced, discrete values.

Multiple Relaxation Times. There are several ways in which a multiplicity of relaxation times can arise. An obvious one can be represented by  $\omega$ -hydroxy acids having lengths great enough that the carbon backbone can be considered relatively flexible. The magnitudes of the separated charges can be considered approximately constant, but the separation of the charges depends on the configuration of the carbon

backbone of the molecule and thus varies in a more or less random manner between two extreme values. The dipole moment thus varies as does the frictional resistance to rotation.

Another common example is that of an ellipsoidal molecule having a dipole which is not aligned with either axis. There are three relaxation times corresponding to the three axes of the ellipsoid. This case has been treated theoretically by Perrin (64) by a fairly simple modification of the Debye equation. Scherer and Testerman used an analogous model to explain the resonance dispersion they observed in solutions of cellulosenitrate (73), and this model has been widely applied to explain the distribution of relaxation times generally found in solutions of polymers. If the axial ratio of the ellipsoid were great enough, the dispersion regions would not overlap.

A very wide distribution of relaxation times would be expected in a flexible polymer because of the wide variance in the size of the chain segment which might tend to follow the field. Superimposed on this would be the effect of an axial ratio close to unity and consequent overlap of the dispersion regions due to the relaxation times along the different axes. Samples of polymers, even fractions, are polydisperse to some extent, so there is a distribution of relaxation times as a result of this also.

The case of multiple relaxation times has been treated mathematically and theoretically in several ways. The easiest to understand is that of Perrin mentioned earlier. This was found adequate by Scherer and Testerman (73). Frohlich has approached the problem from a kinetic

rather than mechanical point of view (27). He assumed that there were two equilibrium positions of the molecule separated by an energy barrier and derived an equation on this basis. He then assumed further that the height of the barrier can depend on the positions of the individual molecules with respect to their neighbors and thus provided a basis for a distribution of relaxation times. The relaxation time for an individual molecule would be the time required for it to make a transition from one equilibrium position to the other.

The distribution of relaxation times in a randomly coiled polymer molecule due to the flexibility of the chain has been studied and treated theoretically by Kirkwood and Fuoss with some success (50). The equations were derived by making assumptions which could only be justified in dilute solutions and then the results were tested by measurements in relatively very concentrated solutions. Qualitative agreement was obtained which was felt to be satisfactory under the circumstances. These authors use a development similar to that of Debye in that they resort to the theory of Brownian movement. It differs in that they evaluate a distribution of relaxation times. It is interesting to note that they obtained a theoretical indication that the critical frequency should be proportional to the degree of polymerization of the polymer. Their ideas were extended somewhat by Hammerle and Kirkwood (37).

The equation which has probably been used more than any other; except, perhaps, the Debye equation itself; is an empirical equation developed by Cole and Cole (12). This approach is characterized by

the introduction of an arbitrary parameter,  $\alpha$ , which represents a measure of the width of the distribution. The distribution itself is somewhat flatter in shape than the normal distribution. The value of the method lies in the fact that  $\alpha$  can be determined very readily from a plot of  $\epsilon'$  against  $\epsilon''$  in the complex plane. If the distribution of relaxation times is extremely narrow, corresponding to a value of zero for  $\alpha$ , the plot takes the form of a semicircle having its center on the real axis and having a diameter equal to  $\epsilon_s - \epsilon_\infty$ .

It has been frequently found that data which does not follow the Debye equations gives a plot which is semicircular but has its center somewhere in the complex plane below the real axis. The angle formed between the real axis and a line through the origin and the center of the semicircle is a simple function of  $\alpha$ . Consequently, it is a relatively simple matter to characterize the apparent width of the distribution of relaxation times, at least approximately. The opinion has been expressed (41) that most of these theoretical distributions (12) (50)(48) differ to such a small extent that they are experimentally indistinguishable.

Another, altogether different, type of dispersion which is called resonance dispersion, is found when the particle which is displaced by the field is elastically bound. The particle would describe damped oscillatory motion when the field was suddenly removed. This situation is analyzed by Frohlich (273). Resonance dispersion is characterized by the fact that it takes place over a much narrower band of frequencies than dispersion involving particles which return to their original

orientation by rotational diffusion. Scherer and Testerman attributed their experimental results to resonance dispersion (73).

It should also be mentioned here that in a recent review of dielectric phenomena in polymer solutions (7), de Brouckere and Mandel point out that there is no theoretical or experimental proof of the exponential decay of polarization, and that it is their opinion that some of the discrepancies between theory and experiment, which are attributed to multiplicity of relaxation times, may be due to the inadequacy of this assumption (8).

The literature on the subject of dispersion and loss has been covered several times in considerable detail. Debye (16), Kauzmann (48), Davies (15), and particularly Smyth (78) cover the subject in considerable breadth and depth. It was reviewed as it applies to high polymer solutions by Fuoss (33)(32) and more recently by de Brouckere and Mandel (7).

Experimental Results. A large amount of experimental work has been done on the problem of dielectric dispersion and loss in polymers. It is unfortunate, from the present point of view, that so little of the available information has any significance with respect to the present investigation.

The interest in polymeric materials as electrical components stimulated interest in the electrical properties of solid polymers. The results of such investigations are quite significant from a practical point of view, but the transfer to solutions of conclusions based on data obtained on plasticized solids seems very risky. This work is

exemplified by the investigations of Fuoss on poly-(vinyl chloride) (31); Funt, et al., on poly-(vinylidene chloride) (29) and on poly-(vinyl acetate) (30); and Girard and Abadie on cellulose acetate and cellulose nitrate (35). In the investigation cited, and (57), Fuoss indicated that the critical frequency,  $f_c$ , should be proportional to the reciprocal of the intrinsic viscosity and was able to get some experimental confirmation of this. Funt and Sutherland also report such a tendency for poly-(vinylidene chloride).

Considerable interest has been shown recently in the correlation of dielectric and mechanical properties, and this has also stimulated investigations on solid polymers. Results of Boyd (6) and Strella (81) are typical of these measurements.

Comparatively little work has been done on polymer solutions and even less has been done on dilute solutions. We will refer here to solutions containing less than one gram of polymer per deciliter as dilute. In principle the term dilute is usually reserved for solutions where the effect of polymer-polymer interactions is negligible. The reason that dilute solutions have not been used more is that the measurements usually are very much easier when carried out on solids and more concentrated solutions. In the case of solids, mechanical manipulation is fairly simple and the change in capacitance is rather large. Even in concentrated solutions the change in capacitance is much larger than in dilute solutions. This makes the measurement easier, because the thing being measured is larger.



Some work has been done on protein solutions. These compounds require highly polar solvents and, consequently, are difficult to handle insofar as the measurements are concerned. In addition to this, the theoretical treatment of solutions involving polar solvents is very difficult. This work has been reviewed by Edsall (21), Oncley (61), and Wyman (93). There are two very interesting aspects of this work. One is that in some of the systems studied, the agreement with the Debye equation for  $\epsilon'$  is excellent (94)(61). The other is that the change in dielectric constant is a function of the concentration and appears to be independent of the molecular weight in many cases.

Solution measurements on polymers have been characterized by high concentrations. Funt and Mason investigated the dielectric behavior of a number of fractions of poly-(vinyl acetate) in toluene (30). The concentrations used were 15, 30, and 40 gm./100 ml. The results resemble those obtained by Fuoss on plasticized poly-(vinyl chloride). More dilute solutions, about 3 gm./100 ml., were used by Scherer and Testerman in their study of the dispersion of cellulose nitrate in acetone (73). Conclusions based on this work have been placed in doubt by the fact that Testerman and Pauley found later that what was actually being measured was a cellulose nitrate-copper complex (64). This must be recognized as an early attempt at relatively dilute solution measurements. More important, however, is the fact that resonance dispersion was found, that the critical frequencies could be related to the molecular weights, and that the shape of the resonance dispersion curve could be related to the molecular weight distribution

curve. This appears to the author to offer some advantage; because, if the mechanical losses were small and the polymer molecules were capable of independent action, the resonance dispersion curve and molecular weight distribution curve might be practically superposable. This is not to be expected in the case of Debye dispersion.

de Brouckere and Mandel have collected a considerable quantity of data on several synthetic polymers in nonpolar solvents (7)(9). They found that, for poly-(vinyl acetate), poly-(methyl methacrylate), poly-(butyl methacrylate) and poly-(vinyl chloride) solutions having concentrations from about 4 to 7 gm./100 ml., the critical frequencies depended on the solvent, the temperature, and perhaps to some extent on the concentration. It was not found to be affected by the molecular weight of the polymer. They conclude that the theoretical and experimental work by Fuoss and Kirkwood is erroneous in this respect.

The dielectric loss in solutions of poly-(oxyethylene glycol) has been studied over a very wide band of frequencies (67). Dioxane and toluene were used as solvents and the concentrations were about 20 gm./100 gm. No low frequency maximum in the loss curve was found. This is not surprising in view of the difficulties accompanying such a measurement. The present writer has found that the very small expected peak in the loss curve for cellulose acetate in dioxane, and ethyl cellulose in benzene and toluene, is completely obscured by other effects. A maximum found at about 6 mc was independent of the molecular weight, which is also not surprising in view of other work.

In addition to the investigations of Fuoss and Testerman mentioned earlier, several cases have been found where the dispersion or loss region depends on the degree of polymerization, DP. The most notable are probably those of Scherer, Levi, and Hawkins (69)(70)(71)(72). They investigated the low frequency dielectric dispersion in dioxane solutions of cellulose acetate at a concentration of about 5 gm./100 ml. Ethyl cellulose was studied in dilute solutions of dioxane, carbon tetrachloride, benzene, toluene, and n-butyl acetate. A linear relationship between  $\log [\eta]$  and  $\log f_c$  was found in each case. The investigation of ethyl cellulose was carried a step past the dilute solution stage by extrapolating the critical frequencies obtained at several low concentrations to zero concentration. The result is called an intrinsic critical frequency,  $[\nu_c]$ , by these authors.

A study of both the dielectric dispersion and loss in poly-(benzyl-L glutamate) by Wada has revealed a linear relation between  $\log f_c$  and  $\log \bar{M}_w$ , the weight average molecular weight (92).

Marchal and his collaborators have studied poly-(vinyl bromide) in tetrahydrofuran and cyclohexenone and found no dependence of the critical frequency on the degree of polymerization, DP, (51). However, the concentrations were 3 gm./100 ml. or higher, the lowest frequency investigated was about 2 mc and the temperatures were in the region of  $-20^\circ \text{C}$ . In view of other results, one could hardly expect to find a DP dependence under such conditions. In other investigations he has concluded that the dipole moment should be related to the DP (54)(55). This has also been shown by Wada (91).

A representative study of polyelectrolytes was carried out by Allgen and Roswall on dilute aqueous solutions of sodium alginate (1). Along with several other variables, the effect of DP was studied and it was found that a relationship existed between the critical frequency and the degree of polymerization.

#### CELLULOSE ACETATE

It is rather amazing that a compound could have been known as long, studied as much, and understood as little as cellulose acetate. The general structure of cellulose has been known for some time (63), although there is still some question concerning the presence and effect of nonglucose units; namely, mannose and xylose (56). It is generally believed, however, that the various anomalies found in cellulose acetate arise as a result of the configuration of the molecule. During the early development of the light scattering technique, several investigations were carried out on cellulose acetate and cellulose nitrate fractions, and it was concluded that the molecule behaved as a rigid rod up to a DP of about a hundred while molecules having a DP greater than 500 could be considered random coils (3)(5)(19)(46)(80). It is noted that the theoretical viscosity relationships based on random coils usually do not hold for these compounds. The relationship between viscosity and DP frequently shows signs of nonlinearity; the intrinsic viscosity is found to vary from one solvent to another to a much greater extent than is found in other polymers; and the variation in intrinsic viscosity seems to depend on unexplained qualities of the solvents. Recent investigations by Flory (25) and Moore (59) and

their co-workers summarize the problem and offer some constructive conclusions. Hermans (42) has suggested that in cellulose itself hydrogen bonds are formed between the -OH group in the 6-position and the glucosidic oxygen on the adjacent ring; whereas, Robinson (65) suggests a hydrogen bond between the primary -OH on one ring and the secondary -OH on the next. Moore and Russell (58) suggest that if hydrogen bonding of this type takes place in cellulose acetate the large changes in intrinsic viscosity from one solvent to another might be due to the ability or inability of a particular solvent to interrupt such hydrogen bonding. They suggest further that some of the difficulties in molecular weight determination might be attributed to association in some solvents due to intermolecular hydrogen bonding. The fact that there have been indications that in the secondary acetate the un-acetylated hydroxyl groups predominate in positions -3 and -6 (34) lends strength to this explanation. However, the fact that the light scattering work mentioned earlier indicated relatively stiff chains for both the trinitrate and the triacetate cannot be easily explained from this point of view. It appears safe to conclude on the basis of the experimental evidence that secondary cellulose acetate is better described as a rigid rod than a random coil up to a DP of at least one hundred.

A complete discussion of the chemistry of the cellulose esters including the acetate is given by Heuser (44).

## METHODS OF MEASUREMENT

Since the present interest is in dielectric dispersion curves and critical frequencies, this section will be limited to consideration of methods of determining dielectric constant and loss as functions of frequency. Most methods of measurement depend upon a knowledge of the mathematical relationship among the components of a circuit under certain electrical conditions, the conditions being chosen in such a way that they are easily recognizable and the mathematical relationships are as simple as possible. The force and calorimetric methods are exceptions, but all of the others described here fall in this category.

Force and Calorimetric Methods. These two methods can be considered together because they are complementary. In the case of the force method the attractive force between two charged bodies in the medium is determined and the dielectric constant calculated by the use of Coulomb's law and the known permittivity of free space. This method is not in common use, but has been used recently with some success (1). It has the disadvantage that only the dielectric constant is measurable, but it has the advantage that the measurement is unaffected by the conductivity of the medium within very wide limits.

The calorimetric method complements the force method because it can be used to determine the dielectric loss irrespective of the dielectric constant of the medium. It consists in the calorimetric determination of the heat liberated in the medium which is placed in a time varying electric field (75). It appears to the author that the

method would be very time consuming because of the necessity for achieving thermal equilibrium at each frequency, but it has the advantage that as long as the field within the medium could be maintained constant (constant amplitude and wave-form) the measurement should be independent of extraneous factors over a very wide range of frequencies.

Bridge Methods. At present bridge methods are finding very general use due to improvements in the design of components and the bridges themselves. In principle a-c bridges are only slightly more complicated than the simple Wheatstone bridges used for d-c measurements. The mathematical relationship among the complex impedances which make up the arms of an a-c bridge is exactly the same as that among the resistances in a Wheatstone bridge. This relationship is fairly simple at balance. The conditions for balance in the a-c bridge are slightly more complicated than they are for a d-c bridge. The voltages at two diagonally opposite corners must have equal amplitudes, must be in phase, and must have the same waveform. The latter condition is approached by using as pure a sine wave input to the bridge as is obtainable. The other conditions are met by balancing the bridge through adjustment of the impedances in one or more of the arms. In order to use a bridge to make precise measurements over a band of frequencies, the components of one of the impedances should be capable of independent adjustment. Thus, in a capacitance bridge, there should be no variation in the residual inductance and resistance as the capacitance of the variable capacitor is varied; and there should be no variation in the

inductance and capacitance as the resistance of the variable resistor is varied. Also, when the effects of the residuals are balanced at one frequency, they should be balanced at all frequencies in the operating range. In practice these requirements cannot be completely satisfied. It is usually possible to counteract the effects of varying residuals by compensation and by minimizing them, but the compensation must be adjusted as the frequency is changed. Many physical and electrical configurations have been suggested, and all have certain advantages and disadvantages under various circumstances. Harris (38), Laws (52), and Hague (36) discuss the subject of bridge measurements in detail in their texts.

An alternative to the bridge method which is very similar in principle was proposed by Tuttle (90) and used by Honnell (45) for the measurement of high resistances at radio frequencies. This consists of the use of a bridged-T network which will be described later and has the practical advantage that the oscillator and null detector have a common terminal which can be grounded. The disadvantages due to residuals remain with this method.

Resonance Method. In this method the mathematical relationship considered is that between frequency, resistance, inductance, and capacitance in a suitable circuit at resonance, and the condition necessary for the relationship to hold is that the circuit be in resonance. There are several possible arrangements of the components and several ways of recognizing the condition of resonance. The circuits and procedure used by Scherer and Testerman are typical of this type of



measurement (73). A parallel resonant circuit consisting of a precision variable capacitor and suitable inductance is loosely coupled to an oscillator operating at some particular frequency and to a circuit capable of measuring the voltage developed in the resonant circuit, while exercising the least possible influence on it. In the investigation cited this consisted of a vacuum tube voltmeter using a light beam galvanometer as the indicator and inductively coupled to a parallel resonant circuit. The variable capacitor could be varied until resonance was indicated at the particular frequency. The unknown capacitor could then be switched in and the change in the capacitance of the precision capacitor necessary to achieve resonance again was noted. This change equalled the capacitance of the unknown cell. This procedure can be extended fairly simply to give the dielectric loss of the cell.

This method has the advantage that fewer components are involved in the measuring circuit, and there is consequently less difficulty with residuals; the sensitivity of the method can be made quite high; and it can be used conveniently from frequencies of ten or twenty kilocycles up to high radio frequencies. The method is relatively useless for samples having appreciable conductivities and is limited to frequencies greater than a few kilocycles for precise work.

The method of measurement used in the present investigation is an adaptation of this procedure based on a resistance-capacitance oscillator.

EXPERIMENTALMATERIALS

Cellulose Acetate. The cellulose acetate used in this investigation came from the Hercules Powder Company, Wilmington, Delaware. The original material is Type PH-1, Lot No. 3681, and has been reported by Hawkins to have a combined acetic acid content of 52.5% and a degree of polymerization of 185 as determined by viscosity measurements(39).

All but one of the fractions used in this investigation were obtained by Levi in order to determine as accurately as possible the molecular weight distribution curve of the original material (53). This fractionation was carried out in connection with another investigation in early 1956. The procedure used was essentially the same as the one used earlier by Hawkins (39) and Thompson (89), except that fractions were not combined during the course of the fractionation, and an attempt was made to recover all of the material originally present. Two complete sets of fractions were obtained and were designated as I-F- and II-F- series. The designations which Levi assigned the fractions will be used except that the series prefix, I-F-, will be omitted. This is permissible, because only the I-F- series of fractions was used in the present investigation, and there is consequently no need to distinguish between the two series here. The designations used consist of two numbers followed by a letter; for example, fraction 31B. This means that the fraction was the third one brought down in the first fractionation, the first one down in the first refractionation, and the second one brought down in the second refractionation.

A total of 59 fractions representing 98.7% of the polymer originally present were obtained. Intrinsic viscosities were used to characterize the individual fractions and the results are given in Table 1.

The viscosity measurements were carried out according to standard procedures at 25° using acetone as the solvent. The fractions in Table 1 which are marked by asterisks were run by the author and all of the rest were run by Levi. The data obtained are collected in Table 2. Fractions 62D, 53B, 61C, 53A, 32B, 12F, and 33B, do not appear in Table 2, because they were found to have the same intrinsic viscosities as fractions 54C, 52D, 62A, 51A, 31C, 42C, and 52A respectively. The weights of the appropriate fractions were combined for the calculation of  $I_p$ , the cumulative weight per cent. Figure 1 is a plot of this data.

The other fraction which will be designated simply as fraction A was obtained by Awni during the course of an earlier investigation, but was not used or reported (2). It was obtained from Type PM-4 cellulose acetate which had been supplied by the Hercules Powder Company, Wilmington, Delaware, and was indicated by Awni to have 50.8% combined acetic acid and a degree of polymerization, DP, of 225 as determined by the reduced viscosity of a 0.1 gm./100 ml. solution in acetone at 25°. The reduced viscosity corresponding to this DP was calculated by means of the same equation which Awni used and was found to be 2.11. The intrinsic viscosity of this fraction was determined in acetone at 25° by the present author and it was found that the reduced viscosity

TABLE 1

Reduced Viscosities of Cellulose Acetate Fractions  
In Acetone at 25°C

Fraction	(c) gm./100ml.	$\eta_{sp}/c$
21A*	0.415	4.10
	0.311	3.57
	0.259	3.33
	0.207	3.20
	0.104	2.77
	0.069	2.62 [n] = 2.32
31A*	0.294	3.19
	0.258	3.12
	0.221	2.94
	0.172	2.81
	0.086	2.56 [n] = 2.27
32A*	0.539	3.47
	0.449	3.19
	0.360	2.97
	0.270	2.75
	0.180	2.48 [n] = 2.02

TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	$N_{sp}/c$
41A	0.375	3.20
	0.300	3.00
	0.200	2.66
	0.120	2.40
	0.064	2.18 $[\eta] = 1.98$
21B*	0.364	2.91
	0.273	2.59
	0.182	2.36
	0.091	2.81 $[\eta] = 1.91$
12B*	0.434	3.44
	0.434	3.41
	0.362	3.06
	0.289	2.87
	0.217	2.65
	0.124	2.34 $[\eta] = 1.90$
41B*	0.368	2.91
	0.295	2.64
	0.196	2.45
	0.118	2.25
	0.098	2.13 $[\eta] = 1.88$

TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	Nsp/c
12C*	0.320	2.99
	0.180	2.48
	0.137	2.31
	0.111	2.27
	0.484	3.57
	0.346	3.06
	0.277	2.82
	0.207	2.53 [n] = 1.64
12A*	0.326	2.79
	0.272	2.65
	0.163	2.33
	0.217	2.44
	0.163	2.27
	0.109	2.18 [n] = 1.83
31B*	0.506	3.24
	0.337	2.77
	0.253	2.55
	0.169	2.30 [n] = 1.84
12D*	0.514	3.54
	0.411	3.08
	0.308	2.74
	0.206	2.41
	0.103	2.18 [n] = 1.77

TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	$\eta_{sp}/c$
	0.541	2.91
	0.451	2.67
22A*	0.361	2.55
	0.271	2.31
	0.180	2.13 $[\eta] = 1.75$
	0.414	2.42
	0.331	2.32
42B	0.221	2.14
	0.132	1.96
	0.071	1.85 $[\eta] = 1.71$
	0.600	3.13
	0.300	2.56
42A	0.200	2.27
	0.150	2.14
	0.100	1.99 $[\eta] = 1.70$
	0.418	2.59
	0.279	2.26
11A*	0.209	2.07
	0.140	1.97
	0.105	1.90 $[\eta] = 1.65$

TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	Nsp/c
12E*	0.538	3.11
	0.385	2.69
	0.308	2.38
	0.231	2.18
	0.154	2.04
	0.077	1.89 $[\eta] = 1.63$
33A	0.539	2.74
	0.360	2.36
	0.216	2.09
	0.180	2.01
	0.116	1.83 $[\eta] = 1.62$
51B	0.342	2.22
	0.274	2.09
	0.183	1.92
	0.137	1.84
	0.091	1.81 $[\eta] = 1.59$
61A	0.442	2.00
	0.294	1.87
	0.235	1.82
	0.154	1.68
	0.107	1.60 $[\eta] = 1.45$



TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	$\eta_{sp}/c$
21C*	0.400	1.89
	0.333	1.81
	0.267	1.75
	0.200	1.66
	0.133	1.57 $[\eta] = 1.44$
52A	0.363	1.86
	0.290	1.77
	0.194	1.66
	0.116	1.54
	0.097	1.54 $[\eta] = 1.41$
33B	0.481	1.97
	0.256	1.74
	0.110	1.53
	0.154	1.58 $[\eta] = 1.41$
42C	0.570	2.06
	0.285	1.72
	0.190	1.61
	0.143	1.55
	0.095	1.47 $[\eta] = 1.37$

TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	$n_{sp}/c$
12F*	0.479	1.99
	0.399	1.93
	0.319	1.81
	0.240	1.67
	0.160	1.58 $[n] = 1.37$
22B	0.553	1.90
	0.461	1.79
	0.369	1.73
	0.276	1.62
	0.184	1.54 $[n] = 1.36$
31C*	0.540	1.97
	0.450	1.82
	0.270	1.61
	0.180	1.53 $[n] = 1.30$
32B*	0.408	1.63
	0.245	1.51
	0.163	1.42
	0.082	1.36 $[n] = 1.30$

TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	$N_{sp}/c$
52B	0.349	1.64
	0.279	1.58
	0.186	1.48
	0.139	1.42
	0.093	1.39 $[\eta] = 1.29$
51D	0.438	1.61
	0.292	1.50
	0.219	1.45
	0.175	1.39
	0.094	1.29 $[\eta] = 1.26$
32C	0.331	1.55
	0.207	1.45
	0.166	1.39
	0.111	1.35
	0.083	1.33 $[\eta] = 1.25$
61B	0.446	1.57
	0.297	1.46
	0.223	1.36
	0.178	1.37
	0.096	1.28 $[\eta] = 1.20$

TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	$N_{sp}/c$
33C	0.502	1.55
	0.335	1.38
	0.251	1.30
	0.201	1.29
	0.167	1.28 $[\eta] = 1.19$
43A	0.400	1.41
	0.267	1.30
	0.200	1.26
	0.133	1.21
	0.086	1.16 $[\eta] = 1.10$
42D	0.395	1.38
	0.316	1.32
	0.211	1.25
	0.127	1.16
	0.083	1.15 $[\eta] = 1.08$
41C	0.448	1.37
	0.179	1.17
	0.143	1.15
	0.077	1.10 $[\eta] = 1.05$

TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	$n_{sp}/c$
51C	0.445	1.31
	0.278	1.27
	0.222	1.26
	0.111	1.13
	0.089	1.10 $[n] = 1.02$
51A	0.304	1.10
	0.190	1.04
	0.152	1.02
	0.114	1.03
	0.070	1.01 $[n] = 0.98$
53A	0.369	1.18
	0.295	1.17
	0.197	1.11
	0.148	1.08
	0.098	1.10 $[n] = 0.98$
52C	0.531	1.14
	0.332	1.07
	0.265	1.04
	0.177	1.00
	0.088	0.95 $[n] = 0.92$

TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	$N_{sp}/c$
62A	0.335	1.00
	0.268	0.99
	0.179	0.96
	0.134	0.93
	0.089	0.90 [n] = 0.88
61C	0.356	0.99
	0.223	0.93
	0.178	0.94
	0.119	0.92
	0.089	0.90 [n] = 0.88
11B*	0.378	0.95
	0.252	0.92
	0.189	0.91
	0.126	0.87
	0.108	0.87 [n] = 0.84
43B	0.396	0.97
	0.317	0.93
	0.211	0.89
	0.127	0.85
	0.083	0.87 [n] = 0.82

TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	$n_{sp}/c$
52D	0.458	0.93
	0.286	0.89
	0.229	0.88
	0.153	0.86
	0.092	0.82 $[n] = 0.81$
53B	0.478	0.99
	0.299	0.93
	0.239	0.88
	0.159	0.87
	0.096	0.85 $[n] = 0.81$
54A	0.415	0.95
	0.332	0.92
	0.221	0.87
	0.166	0.86
	0.087	0.83 $[n] = 0.80$
22C*	0.593	0.81
	0.494	0.78
	0.395	0.78
	0.297	0.76
	0.198	0.75 $[n] = 0.72$

TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	$n_{sp}/c$
53C	0.336	0.74
	0.163	0.71
	0.112	0.70
	0.084	0.69 $[n] = 0.68$
61D	0.362	0.70
	0.226	0.69
	0.181	0.67
	0.121	0.67
	0.091	0.65 $[n] = 0.65$
63A	0.361	0.70
	0.226	0.66
	0.181	0.66
	0.120	0.67
	0.090	0.64 $[n] = 0.63$
33D	0.634	0.69
	0.238	0.61
	0.317	0.63
	0.159	0.61
	0.106	0.60 $[n] = 0.59$



TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	$N_{sp}/c$
62B	0.353	0.63
	0.283	0.61
	0.189	0.59
	0.141	0.60
	0.094	0.59 $[\eta] = 0.57$
54B	0.398	0.51
	0.249	0.47
	0.199	0.47
	0.149	0.47
	0.092	0.43 $[\eta] = 0.42$
43C	0.412	0.43
	0.330	0.42
	0.220	0.40
	0.132	0.39
	0.086	0.40 $[\eta] = 0.38$
62C	0.346	0.38
	0.277	0.36
	0.185	0.37
	0.139	0.37
	0.092	0.36 $[\eta] = 0.36$

TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	Nsp/c
	0.107	0.31
54C	0.093	0.31
	0.075	0.29 $[\eta] = 0.29$
	0.377	0.32
	0.283	0.31
62D	0.226	0.32
	0.189	0.30
	0.121	0.30 $[\eta] = 0.29$
	0.384	0.32
	0.307	0.32
62E	0.205	0.31
	0.154	0.31
	0.103	0.28 $[\eta] = 0.28$
	0.422	0.27
	0.281	0.27
63B	0.211	0.26
	0.169	0.26
	0.090	0.25 $[\eta] = 0.24$

TABLE 1 (Cont.)

Fraction	(c) gm./100 ml.	Nsp/c
	0.502	3.32
	0.335	2.63
A*	0.167	2.19
	0.084	2.09 [n] = 1.70

TABLE 2

Data for Molecular Weight Distribution  
Curve of Original Material

Fraction	Weight	$I_p$	n
63B	2.4	1.2	0.24
62E	1.2	3.0	0.28
54C	2.7	5.0	0.29
62C	1.0	6.9	0.36
43C	0.9	7.9	0.38
54B	0.2	8.4	0.42
62B	1.4	9.2	0.57
33D	1.1	10.5	0.59
63A	0.9	11.5	0.63
61D	0.6	12.3	0.65
53C	0.4	12.8	0.68
22C	0.4	13.2	0.72
54A	0.6	13.7	0.80
52D	1.4	14.7	0.81
43B	1.3	16.1	0.82
11B	0.1	16.8	0.84
62A	2.0	17.8	0.88
52C	0.5	19.1	0.92
51A	2.1	20.4	0.98
51C	0.4	21.7	1.02

TABLE 2 (Cont.)

Data for Molecular Weight Distribution  
Curve of Original Material

Fraction	Weight	$I_p$	$[\eta]$
41C	1.0	22.4	1.05
42D	1.1	23.5	1.08
43A	2.3	25.2	1.10
33C	0.9	26.8	1.19
61B	1.2	27.9	1.20
32C	0.4	28.7	1.25
51D	0.8	29.3	1.26
52B	2.5	31.0	1.29
31C	0.6	32.5	1.30
22B	0.5	33.1	1.36
42C	8.5	37.6	1.37
52A	5.6	44.8	1.41
21C	0.4	47.8	1.44
61A	2.3	49.4	1.45
51B	3.7	52.7	1.59
33A	1.5	55.4	1.62
12E	1.5	56.9	1.63
11A	1.4	58.4	1.65
42A	4.2	61.2	1.70
42B	5.1	65.9	1.71

TABLE 2 (Cont.)

Data for Molecular Weight Distribution  
Curve of Original Material

Fraction	Weight	$I_p$	$[\eta]$
22A	0.5	68.7	1.75
12D	2.3	70.2	1.77
12A	0.5	71.6	1.83
12C	8.2	76.0	1.84
41B	6.3	83.3	1.88
12B	1.8	87.4	1.90
21B	0.7	88.7	1.91
41A	2.5	90.3	1.98
32A	3.0	93.1	2.02
31A	3.6	96.5	2.27
21A	1.7	99.1	2.32
Original Material			1.39

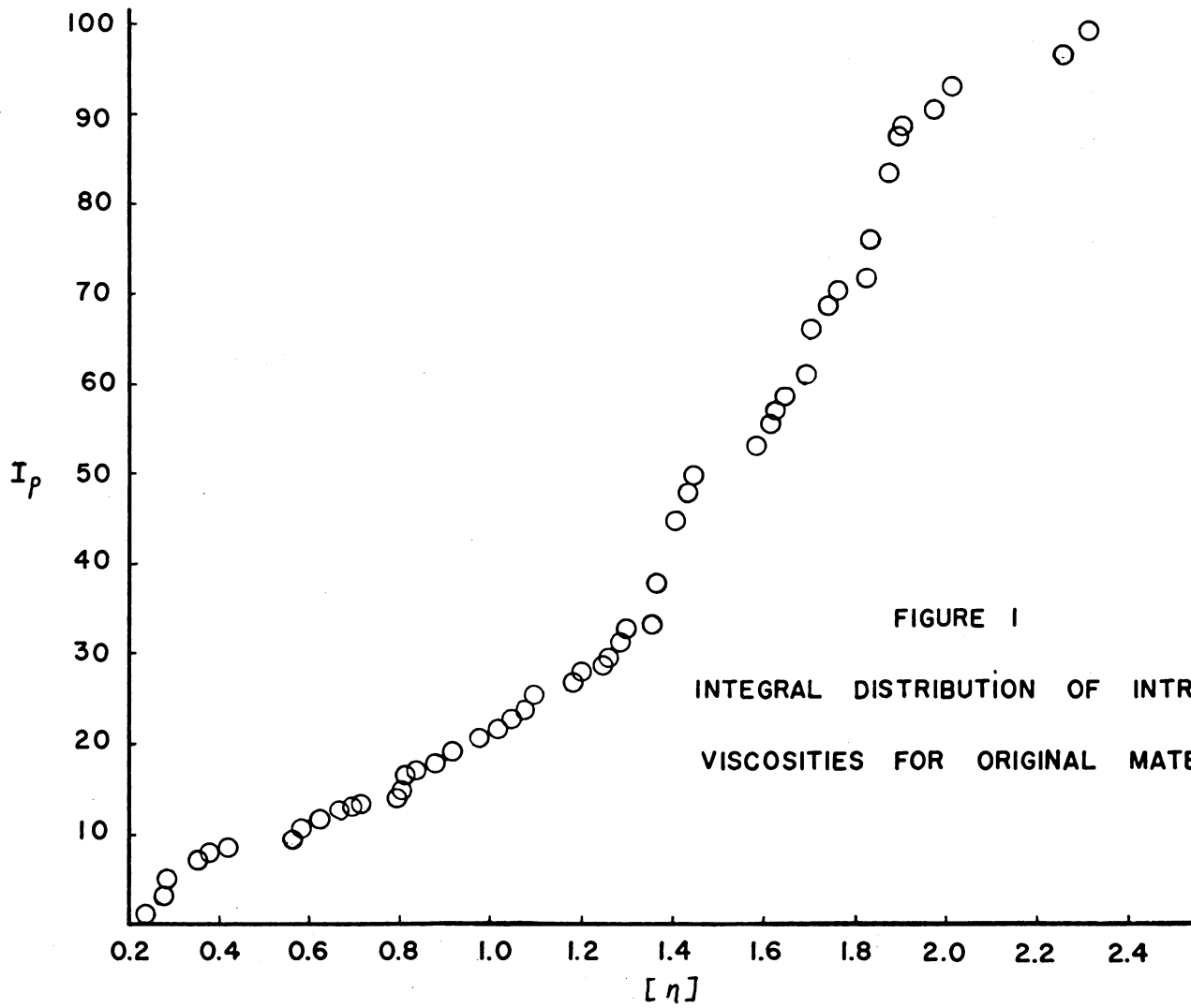


FIGURE I  
 INTEGRAL DISTRIBUTION OF INTRINSIC  
 VISCOSITIES FOR ORIGINAL MATERIAL

versus concentration curve crossed the 0.1 gm./100 ml. concentration line at a reduced viscosity of about 2.10. This is remarkable agreement and is taken as an indication that this fraction had not degraded in storage. It should thus be just as sharp as when it was originally obtained.

Solvents. The acetone used as solvent in the viscosity determinations was C.P. grade and was obtained from the Commercial Solvents Corporation, Newark, New Jersey. No attempt was made to purify the acetone any further, but care was exercised to prevent absorption of water from the air after it was withdrawn from the drum.

The dioxane was a technical grade originally supplied by Carbide and Carbon Chemicals Company, Charleston, West Virginia. Hawkins had found earlier that highly purified dioxane gave the same results as the technical grade in dielectric investigations (39), and this seemed to be true when this investigation was begun. It was found later, however, that considerable improvement could be brought about by purification of the dioxane, and all of the measurements reported were made in solutions of purified dioxane.

The purification was carried out by refluxing the dioxane with metallic sodium for a period of 24 hours and then distilling it. The fraction of the distillate retained boiled in a range of about  $0.5^{\circ}$  and was found to give satisfactory results (24).

Preparation of Blends. In order to supplement the information obtainable from the dispersion curve on the original material, three



blends were prepared and the dielectric dispersion curves of their solutions determined.

In order to keep everything as simple as possible and thus to reduce the number of variables, these blends were prepared in such a way that the differential distribution based on intrinsic viscosities was given by the equation

$$f([\eta]_1) = \frac{1}{b \sqrt{2\pi}} e^{-\frac{([\eta]_1 - m)^2}{2b^2}} \quad (9)$$

where  $[\eta]_1$  is the intrinsic viscosity of the 1<sup>th</sup> species,  $m$  is the value of  $[\eta]_1$  at the point where  $f([\eta]_1)$  is a maximum, and  $b$  is a constant which determines the width of the distribution (13). A value of 1.31 was chosen for  $m$  for all three blends while values of 0.34, 0.25, and 0.16, were chosen for  $b$  in Blends I, II, and III, respectively.

A graphical method was used to determine the amount of each fraction required. This consisted of first plotting the theoretical curve for the particular values of  $m$  and  $b$ . These curves are shown in Figure 2 for the three blends. Beginning at the ends and working toward the center, fractions were chosen at close intervals along the abscissa. This was done in such a way that the sum of the products of the height,  $h$ , of the ordinate at the particular values of  $[\eta]_1$  and  $[\eta]_1 - m$  on the two sides of the maximum point remained as equal as possible. This was done to prevent the curve from becoming skewed, and to assure that the average intrinsic viscosity would fall at the maximum point. After all the fractions were chosen, the values of  $h$  were added

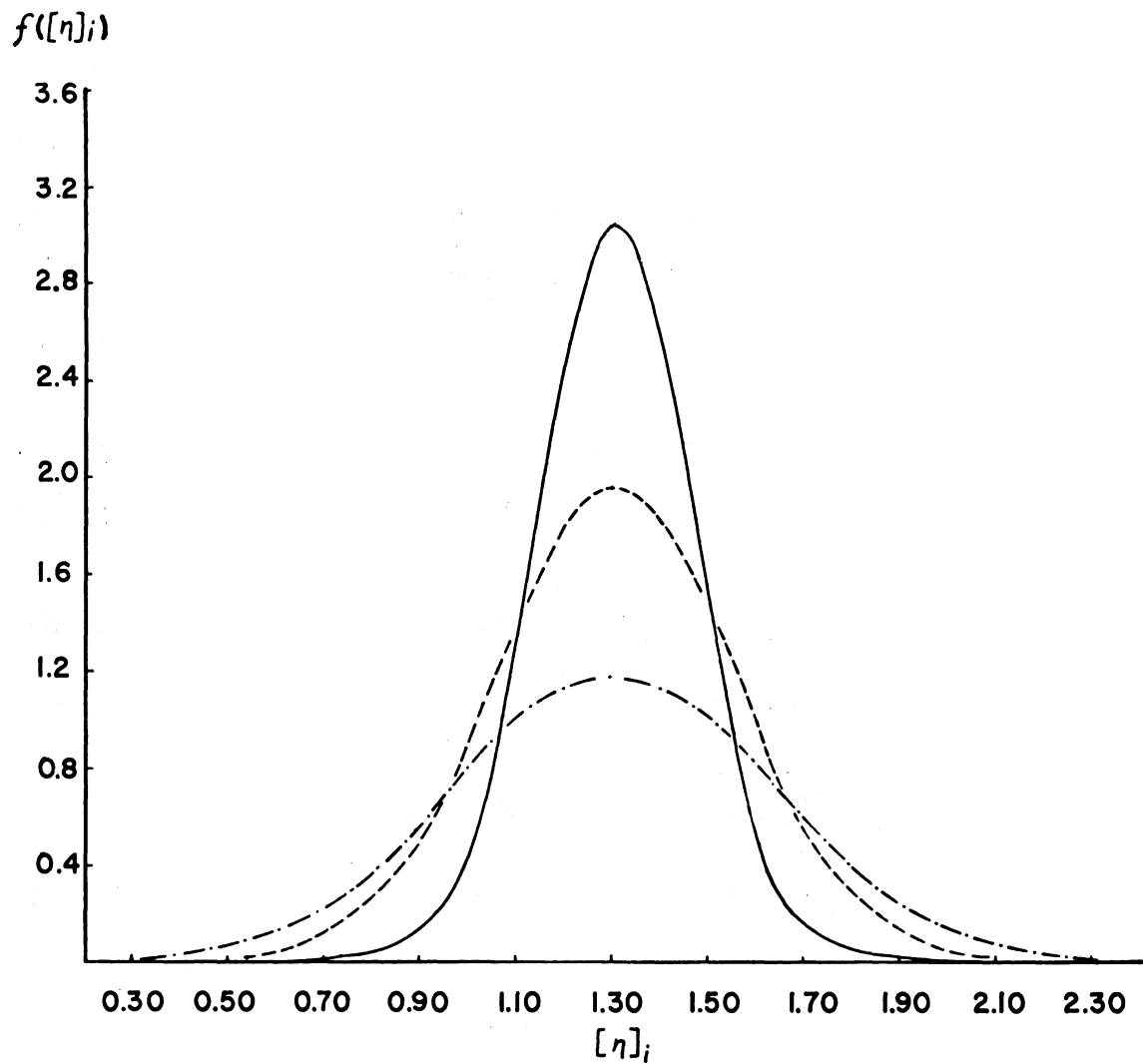


FIGURE 2

THEORETICAL DISTRIBUTIONS OF BLENDS

- BLEND I
- .- BLEND II
- BLEND III

to give  $H$  and the weight fractions,  $W_i$ , of each species were then determined by the ratio of  $h$  to  $H$ . The weight average intrinsic viscosity is given by the sum of all the values of the product  $W_i [\eta]_i$  and was found to be 1.31 for all three blends, within the limits of experimental error. The product of  $W_i$  and the total weight of blend required gave the number of grams of fraction which should have been added.

The data for Blend I is given in Table 3. In this and the following tables  $h$  and  $W_i$  represent calculated values of the ordinate and weight fraction corresponding to the appropriate values of  $[\eta]_i$ .

$h^*$  and  $W_i^*$  are calculated from the weights of the fractions combined in the blends and thus represent actual values of these quantities.

The procedure used in the preparation of Blend I differed somewhat from that used for the other two. In the former case, the fractions were placed in evaporating dishes and exposed to the atmosphere for about 48 hours. Samples were then weighed out to within one milligram of the correct weight, placed in weighing bottles, dried one hour at  $105^\circ$ , cooled in a desiccator, and reweighed. It was hoped that the dry weight would be a constant fraction of the wet weight for all of the fractions. This was found to be only approximately true. A distribution curve drawn on the basis of these weights did not differ significantly from the theoretical curve, however.

The fractions for Blends II and III were placed in weighing bottles, dried, cooled, and the required amount weighed out by difference.

TABLE 3  
Data for the Preparation of Blend I

Fraction	[n]	h	$W_1$	$h^*$	$W_1^*$
54B	0.42	0.04	0.0021	0.03	0.002
62B	0.57	0.11	0.0068	0.10	0.007
63A	0.63	0.16	0.0077	0.13	0.009
61D	0.65	0.18	0.0110	0.16	0.011
53C	0.68	0.21	0.0137	0.20	0.014
54A	0.80	0.39	0.0253	0.37	0.025
62A	0.88	0.53	0.0363	0.53	0.036
52C	0.92	0.61	0.0411	0.60	0.041
53A	0.98	0.74	0.0507	0.74	0.051
41C	1.05	0.87	0.0650	0.95	0.065
43A	1.10	0.96	0.0657	0.96	0.066
61B	1.20	1.12	0.0780	1.14	0.078
51D	1.26	1.16	0.0801	1.17	0.080
32B	1.30	1.17	0.0301	0.44	0.030
22B	1.36	1.16	0.0780	1.14	0.078
52A	1.41	1.13	0.0753	1.10	0.075
61A	1.45	1.08	0.0719	1.05	0.072
51B	1.59	0.83	0.0568	0.83	0.057
12E	1.63	0.75	0.0520	0.76	0.052
42A	1.70	0.62	0.0431	0.63	0.043

TABLE 3 (Cont.)

Data for the Preparation of Blend I

Fraction	$[\eta]$	h	$W_1$	$h^*$	$W_1^*$
22A	1.75	0.52	0.0370	0.54	0.037
12C	1.84	0.36	0.0233	0.34	0.023
21B	1.91	0.25	0.0192	0.28	0.019
41A	1.98	0.17	0.0130	0.19	0.013
32A	2.02	0.14	0.0110	0.16	0.011
31A	2.27	0.02	0.0027	0.04	0.003
21A	2.32	0.02	0.0021	0.03	0.002

It was found that the moisture absorbed by the polymer during the process of weighing was not great enough to introduce a significant error. The data used for the preparation of Blends II and III are given in Tables 4 and 5.

In order to eliminate the possibility of misunderstanding, it should be pointed out that the distributions of these blends are not given by the theoretical curves with the accuracy that the data of Tables 3, 4, and 5, seem to indicate. The fact that the fractions used in the preparation of the blends have distributions of appreciable width, which are probably skewed, and which are not the same from one fraction to another, reduces the accuracy of this method to a level comparable to that which can be attained in the best fractionations.

TABLE 4

Data for the Preparation of Blend II

Fraction	$[\eta]$	h	$W_1$	$h^*$	$W_1^*$
63A	0.63	0.05	0.0021	0.04	0.0022
53C	0.68	0.08	0.0042	0.08	0.0044
54A	0.80	0.24	0.0141	0.27	0.0139
43B	0.82	0.28	0.0167	0.32	0.0168
52C	0.92	0.59	0.0287	0.55	0.0285
53A	0.98	0.82	0.0433	0.83	0.0431
41C	1.05	1.15	0.0590	1.13	0.0592
43A	1.10	1.36	0.0695	1.33	0.0695
33C	1.19	1.73	0.0877	1.68	0.0877
32C	1.25	1.90	0.0956	1.83	0.0958
52B	1.29	1.94	0.0971	1.86	0.0973
22B	1.36	1.91	0.0950	1.82	0.0950
52A	1.41	1.80	0.0893	1.71	0.0892
61A	1.45	1.66	0.0809	1.55	0.0812
51B	1.59	1.05	0.0533	1.02	0.0534
33A	1.62	0.90	0.0480	0.92	0.0482
11A	1.65	0.77	0.0402	0.77	0.0402
42B	1.71	0.54	0.0298	0.57	0.0300
31B	1.84	0.20	0.0334	0.64	0.0333
21B	1.91	0.12	0.0089	0.17	0.0088
32A	2.02	0.04	0.0031	0.06	0.0029

TABLE 5  
Data for the Preparation of Blend III

Fraction	$[\eta]$	h	$W_1$	$h^*$	$W_1^*$
43B	0.82	0.03	0.003	0.01	0.003
53A	0.98	0.36	0.019	0.42	0.019
41C	1.05	0.82	0.040	0.89	0.040
43A	1.10	1.27	0.064	1.42	0.064
33C	1.19	2.32	0.104	2.31	0.104
61B	1.20	2.40	0.110	2.45	0.110
51D	1.26	2.98	0.128	2.85	0.128
52B	1.29	3.03	0.132	2.94	0.132
12F	1.37	2.88	0.120	2.67	0.120
52A	1.41	2.49	0.108	2.40	0.108
61A	1.45	2.10	0.089	1.98	0.089
51B	1.59	0.64	0.033	0.73	0.033
33A	1.62	0.46	0.023	0.51	0.023
11A	1.65	0.32	0.016	0.36	0.016
42B	1.71	0.13	0.009	0.20	0.009
31B	1.84	0.01	0.003	0.07	0.003



## APPARATUS

Quantity to be Measured. The apparatus used here, evolved directly from consideration of the quantity to be measured and the materials available. The stated object was the measurement of dielectric dispersion in solutions of cellulose acetate, but the real interest was not so much in the total behavior of these solutions as it was in the part of the total which could be attributed to the presence of the polymer. It was more or less the same situation as in the measurement of viscosities of polymer solutions, where the absolute viscosity is usually of much less interest than the relative increase in viscosity due to the polymer molecules (4). Thus it was decided that the apparatus would only need to be capable of measuring the difference in the dielectric constants of the solution and solvent over the necessary frequency range. This simplified the task greatly.

Further simplification was made possible by shifting to an evaluation of dielectric dispersion rather than the dielectric constant itself. As pointed out earlier, the dispersion is a function of the change in dielectric constant, and thus was of the same interest as the dielectric constant. The advantage in considering dispersion rather than the dielectric constant lay in the fact that accurate evaluation of the capacitance of the empty cells and other cell constants was made unnecessary; and, in the case of the present apparatus, the calculations were simplified.

The problem was thus resolved to one of measuring the difference between the capacitance of one dielectric cell filled with solvent and the capacitance of another, identical one filled with solution over the frequency range of interest with the necessary precision.

Any of the methods which were discussed in the "Literature Review" could conceivably have been used for such a measurement, but all had certain disadvantages of one kind or another. The resonance method was the most attractive, but it had the obvious and apparently insurmountable disadvantage of being applicable only to relatively high frequencies. This limitation was imposed by the size of the inductors and precision variable capacitors which were available. The possibility of applying a method which is similar enough to the resonance method to be called a modified resonance procedure occurred to the writer while perusing the construction manual and circuit diagram of a Heath Model AG-9 Audio Generator (40).

General Discussion of the Resistance-Capacitance Oscillator. A simplified schematic of a resistance-capacitance oscillator is given in Figure 3. The labeling of the parts follows that of the complete schematic given in Figure 4. The frequency of oscillation is determined by resistors and capacitors rather than the more common inductors and capacitors. This oscillator can be explained most simply by breaking it down into sections according to function as has been done by Edson (23).

Consider first the amplifier consisting of V108, V109, and some of the associated circuitry. It can be seen that the V108 stage is

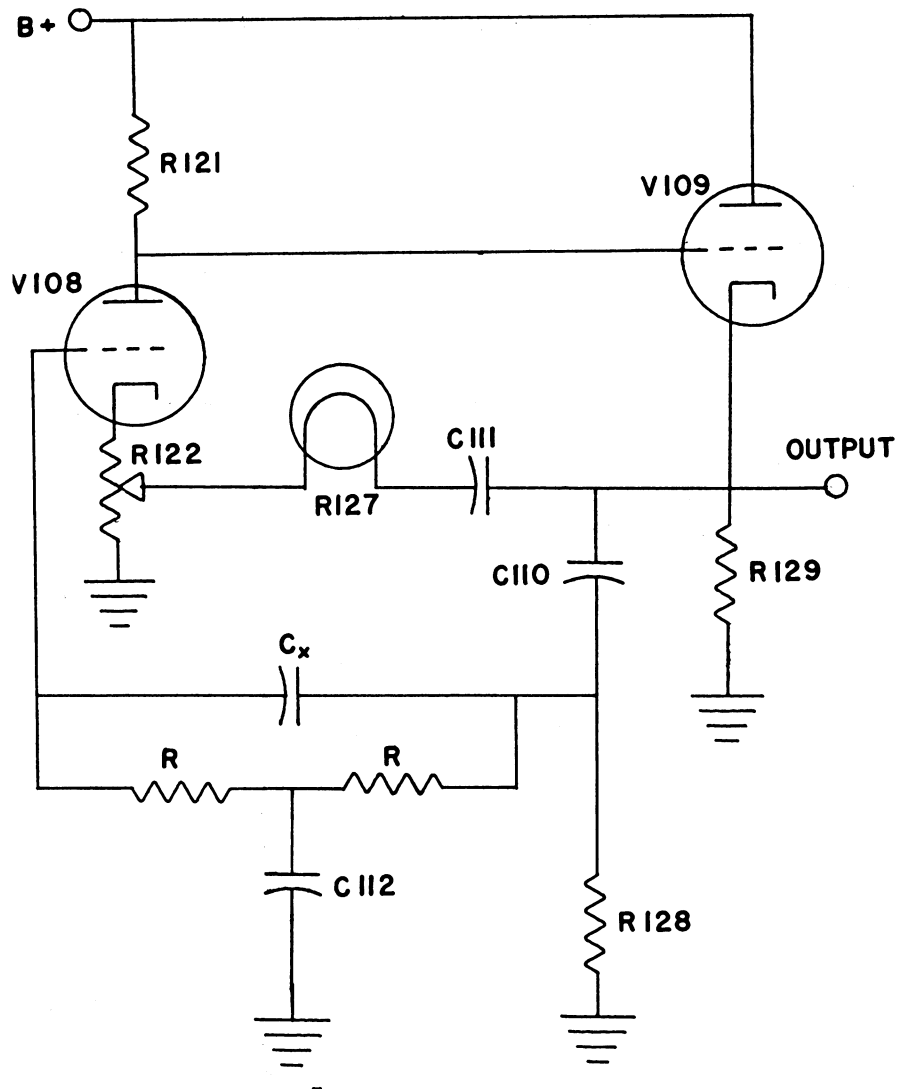


FIGURE 3

SIMPLIFIED SCHEMATIC OF A  
RESISTANCE-CAPACITANCE OSCILLATOR

a voltage amplifier stage, R121 being the plate load resistor, R122 the cathode-bias resistor; and the grid-leak consisting of the series combination, R, R, and R128. The purpose of the cathode follower, V109, is to match the impedance of the amplifier to the load and to decouple V108 from the load so that changes in the load will not affect the important parameters of the overall amplifier. (The input impedance of the amplifier is the most important of these parameters.)

The other circuit components shown in Figure 3 are part of two separate feedback paths from the output of the amplifier to its input. One of these paths is comprised of a capacitor, C111, and a tungsten filament lamp, R127. This is a positive feedback path, and the amplifier becomes an oscillator whenever the signal fed back through this path attains such a magnitude that the gain of the over-all loop represented by the amplifier and all of the feedback paths is unity. Potentiometer R122 controls the attenuation, so it can be used to bring the amplifier in and out of oscillation and to manually control the amplitude of oscillation. It is called the oscillator control.

The other components in the diagram in Figure 3 comprise a degenerative, or negative, feedback path. The operation of this path is not as simple as the regenerative feedback path. For the purposes of the present discussion, R128 can be disregarded because its resistance is high compared to the output impedance of the V109 stage and the impedance of C110. Its only purpose is to serve as

a grid-leak path for V108. The impedance of capacitor C110 is very small compared to the impedance of the network represented by Cx, C112, and the two R's. Its purpose is to prevent the d-c voltage on the cathode of V109 from appearing at the grid of V108 and need not be considered further.

The important components are thus seen to be Cx, C112, and the two resistors labeled R. This network is frequency selective. This means that the signal at the grid of V108 has a magnitude and phase, when compared to the signal across R129, which depend on the frequency. For a given set of values of the components there will be a certain frequency at which the phase shift is zero and the attenuation is a maximum. This is very important. If the amplifier were made to oscillate by introducing positive feedback only, the frequency would be uncontrolled. The output would consist of a band of frequencies having a width limited only by the pass-band of the amplifier. The introduction of a frequency selective negative-feedback path, however, changes the situation markedly.

Assume that the bridged-T network is taken out of the circuit for the moment by placing a jumper from the grid of V108 to ground, and that R122 has been adjusted to provide just enough positive feedback to produce sustained oscillation. Now, if the jumper is removed, oscillation will cease because a signal, which is in phase with the signal on the cathode, will be supplied to the grid through the negative-feedback path. The magnitude of the signal fed back to the grid is a function of frequency, so there will be a frequency

where it is a minimum. If R122 is readjusted so that oscillation begins again, it will be found that only a single frequency is produced.

This can be explained in the following manner. Oscillation occurs when the over-all loop gain is unity. The signal supplied to the grid by the negative feedback path tends to decrease the loop gain; that is, the greater the signal fed back, the less is the loop gain. The magnitude of this signal, however, is frequency dependent; so the loop gain is frequency dependent and can have a value of unity at one frequency while having a lower value at all other frequencies. Therefore, sustained oscillation occurs at a single frequency.

In practice it is impossible to attain and maintain a loop gain of unity by manually adjusting the oscillator control; consequently, some means of automatic control, or limiting, of the amplitude is necessary. In order for oscillation to commence, the net voltage amplification around the closed loop must be greater than unity; and, in order for oscillation to be maintained at a given level, the loop amplification must be exactly unity. If linear resistors and capacitors were used, the amplitude of oscillation would increase until the loop amplification was decreased to unity by the nonlinearity of the amplifier. Such operation is generally undesirable in this type of oscillator because it produces nonlinear distortion of the output wave form. It is particularly undesirable for the present application, because the amplifier parameters vary

rapidly in the nonlinear region. Limiting which does not produce serious nonlinear distortion is accomplished in this instance by means of a nonlinear resistor, the tungsten filament lamp, R127. The resistance of this device increases as its current increases. Thus, as the output voltage rises, this nonlinear resistance increases, and the proportion of the output voltage fed back to the cathode of V108 is reduced. In this way the loop gain is maintained at unity and the amplifier is operated in a linear region.

There are several other ways in which limiting action can be achieved, but this one was chosen because it seemed that it would provide the necessary amount of limiting while having the least influence on the parameters of the amplifier. The input impedance of the amplifier is a particularly important parameter, for example, and every effort had to be made to insure that it was kept constant.

The thermal characteristics of the lamp are of considerable importance in the operation of the oscillator. The thermal inertia should be great enough that the temperature of the filament does not change appreciably with sinusoidal variation of the instantaneous value of the voltage at the lowest frequency of operation. On the other hand, the thermal inertia should be as small as possible so that the time required for the attainment of equilibrium is minimized.

The general statement can also be made that oscillation occurs when the loop phase shifts all cancel. It is generally assumed that this condition is met when the phase shifts in the frequency

selective network is zero, since every effort is made to reduce the phase shifts in the amplifier and the positive feedback path to zero. If it is assumed that these phase shifts are exactly zero, and that the input impedance of the grid of V108 is infinite while the output impedance of V109 is zero; it can be shown by ordinary circuit analysis that the frequency of oscillation is given by:

$$f = \frac{1}{2 \pi R [(C_x)(C_{112})]^{1/2}} \quad (10)$$

The rate of change of the attenuation with frequency depends on the ratio of C112 to Cx; and, in order to achieve reasonable frequency stability, this ratio should have a value of about ten or greater (68)(85).

A general discussion of oscillators along with a detailed mathematical analysis of their operation has been given by Edson (22). Oscillators of the type of interest in the present investigation are discussed by Sulzer (83)(84) and Scott (76).

Development of Apparatus. One method of attack would have been to place the calibrated capacitor in parallel with the cells in one of the capacitive branches of the bridged-T network, but the necessary change in Cp would have been the same as the change in the cells and would have required a precision capacitor calibrated in units at least as small as 0.01 uuf. A second alternative was to place the calibrated capacitor in series with the cells. This had been suggested by Strella (82) in connection with some earlier work and had the advantage that the desired sensitivity could be attained using the cells having a nominal air



capacitance of 100 uuf which were available. The capacitor labeled Cx in Figure 3 would thus consist of a precision variable air capacitor in series with the cell containing solvent, CxI, or the cell containing solution, CxII. There was a serious problem, due to the calibrated capacitor being constructed with its rotor connected to its shield, but this was overcome by insulating the shield from ground and designing the cathode follower stage to give as low an output impedance as was practically possible. The latter precaution was necessary to avoid the deleterious effects of a phase shift introduced by the capacitance of the shield of the precision capacitor to the shielding around the whole network. This led to the configuration shown in the complete circuit diagram of Figure 4.

This schematic is conventional in all respects. Values of the components and other pertinent information which were available to the writer are given in Table 6. In some cases this information was very incomplete because the components were unmarked and of unknown or questionable origin. The voltages given in Table 7 were measured with a carefully calibrated Heath VTVM, Model V-7, between the socket terminal and the chassis under the conditions indicated. These will vary over a considerable range as components, particularly vacuum tubes, are replaced and change due to aging.

If the capacitance of the precision capacitor,  $C_p$ , is called  $C_{pI}$  or  $C_{pII}$  according to whether CxI or CxII is in the circuit; the procedure can be outlined as follows:

TABLE 6  
Description of Components  
of Oscillator  
(Resistors)

Components	Description	Components	Description
RL01	About 0.10, Resistance wire	RL23 and RL26	Ganged 500K, Potentio- meters, General Radio Type 978U
RL02	About 2.00, Resistance wire	RL24 and RL25	Ganged 20K, Wire-wound potentiometer
RL03	5.0, Potentiometer, Ohmite Type H	RL27	115v, eW, Tungsten filament lamp
RL04	45K, 20 Watt, Wire- wound	RL28	47K, $\frac{1}{2}$ Watt
RL05	1.2M, $\frac{1}{2}$ Watt	RL29	12K, 10 Watt, Wire- wound
RL06	1.0M, $\frac{1}{2}$ Watt	RL30	10K, Wire-wound potentiometer
RL07	100, Wire-wound potentiometer	RL31	47K, $\frac{1}{2}$ Watt
RL08	68, $\frac{1}{2}$ Watt*	RL32	100K, 2 Watt
RL09	68, $\frac{1}{2}$ Watt*	RL33	1.0K, $\frac{1}{2}$ Watt
RL10	2.2K, $\frac{1}{2}$ Watt	RL34	1.0K, $\frac{1}{2}$ Watt
RL11	2.2K, 2 Watt	RL35	10K, 2 Watt
RL12	180K, 2 Watt	RL36	100K, $\frac{1}{2}$ Watt
RL13	22K, 2 Watt	RL37	10K, $\frac{1}{2}$ Watt
RL14	470K, $\frac{1}{2}$ Watt		
RL15	4.7K, $\frac{1}{2}$ Watt		

\*Denotes matched pairs.

TABLE 6 (Cont.)  
 Description of Components  
 of Oscillator  
 (Resistors)

Components	Description	Components	Description
R116	500K, Potentiometer	R138	10K, $\frac{1}{2}$ Watt
R117	100K, $\frac{1}{2}$ Watt	R139	10K, $\frac{1}{2}$ Watt
R118	100K, Potentiometer	R140	10K, Potentiometer
R119	330K, $\frac{1}{2}$ Watt	R141	4.7K, $\frac{1}{2}$ Watt
R120	15K, 10 Watt	R142	1.0K, $\frac{1}{2}$ Watt
R121	47K, 2 Watt		
R122	600, Potentiometer		

All values in ohms  
 K indicates X1000  
 M indicates X1000000

TABLE 6 (Cont.)  
Description of Components  
of Oscillator  
(Capacitors)

Components	Description
C101	0.5, 1000 vdc, Oil
C102	12, 700 vdc, Electrolytic
C103	12, 700 vdc, Electrolytic
C104	0.1, 600 vdc
C105	0.1, 600 vdc
C106	0.05, 600 vdc
C107	2.0, 600 vdc, Oil
C108	0.25, 200 vdc, Paper
C109	20, 350 vdc, Electrolytic
C110	0.25, 600 vdc, Paper
C111	0.1, 600 vdc
C112	0.003, Mica
C113	0.003, Mica
C114	2.0, 400 vdc, Oil
Cp	Variable capacitor General Radio Type 722-N

All capacitances are in microfarads.

TABLE 6 (Cont.)

Description of Components  
of Oscillator  
(Miscellaneous)

Components	Description
T101	Plate transformer 1100 vct
T102	Filament transformer
	W-1 6.3 v. at 0.6 a.
	W-2 6.3 v. at 0.6 a.
	W-3 5.0 v. at 6.0 a.
	W-4 6.3 v. at 6.0 a.
L101	Filter choke, 4.5 H at 150 ma dc
L102	Filter choke, rating unknown
SW101	DPST Line switch
SW102	SPST B <sup>+</sup> switch
SW103	9 poles, 3 pos, Wafer switch
SW104 and SW105	Taper pins and lugs (see Text)
F101	1 amp Slo-Blo
F102	1 amp Slo-Blo

TABLE 6 (Cont.)  
 Description of Components  
 of Oscillator  
 (Miscellaneous)

Components	Description
B101	6 volt, Lead cell, Storage battery
D101	Selenium rectifier, Radio Receptor, Type HCD
I101	Pilot light, No. 47
V101	Full-wave vacuum Rectifier
V102	Medium-mu triode, type 6C4
V103 & V104	Gas regulator, type OA2
V105	Low-mu twin triode, type 6BX76T
V106	Sharp cut-off pentode, type 6AU6
V107	Gas regulator, type OA2
V108	Sharp cut-off pentode, type 6AU6
V109	Medium-mu triode, type 6S4
V110A	Medium-mu triode, type 6CM7, T1
V110B	Medium-mu triode, type 6CM7, T2

TABLE 6 (Cont.)  
Description of Components  
of Oscillator  
(Miscellaneous)

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Components	Description
Meter	Weston, 200 ua full scale
CR101-CR103	Crystal diodes, Heath Company part no. 56-1

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TABLE 7  
 Voltages at Vacuum Tube Sockets  
 in the Oscillator

Tube	Pin 1	Pin 2	Pin 3	Pin 4	Pin 5	Pin 6	Pin 7	Pin 8	Pin 9
V101	NC	510	NC	550ac	NC	550ac	NC	510	
V102	500	0	H**	H	500	410	380		
V103	150	0	IC	0	150	IC	0		
V104	300	150	IC	150	300	IC	150		
V105	430	500	440	320	515	440	H	H	
V106	-2.8*	0*	H	H	120*	44*	0*		
V107	150	0	IC	0	150	IC	0		
V108	0	3.0	H	H	270	150	3.0		
V109	IC	273	270	H	H	270	IC	IC	440
V110	510	NC	4.0	H	H	135	0	130	150

\*\* Heaters biased at 300 vdc.

Conditions:

R122 full ccw position

R130 full ccw position

100K ohms from grid of v108 to ground

No external load

Line voltage at 115

All measurements made from pin indicated to chassis except those marked \* which were made to pin 2 of v106.





(1) With C<sub>xI</sub> in the circuit and C<sub>p</sub> set to C<sub>pI</sub>, the resistance was adjusted to the nominal frequency, f<sub>1</sub>.

(2) This frequency was determined with a precision of approximately three parts in 10<sup>5</sup> or better.

(3) C<sub>xII</sub> was switched in and C<sub>p</sub> adjusted to give exactly the same frequency as was found in step (2). The value of C<sub>p</sub> when this frequency was reached was C<sub>pII</sub>.

(4) C<sub>xI</sub> was switched in, C<sub>p</sub> returned to C<sub>pI</sub>, and the frequency checked to make sure it had not changed more than the allowable amount from its original value. If it had not, the resistance was adjusted to give the next nominal frequency, f<sub>2</sub>, where the procedure was repeated.

If the series combination of C<sub>xI</sub> and C<sub>pI</sub> give the same output frequency as the combination of C<sub>xII</sub> and C<sub>pII</sub>, the total capacitances represented by these combinations must be equal. This can be written as:

$$\frac{1}{C_{pI}} + \frac{1}{C_{xI}} = \frac{1}{C_{pII}} + \frac{1}{C_{xII}} \quad (11)$$

A frequency of 400 c could be reached using 500 000 ohm potentiometers. Although the earlier work on concentrated solutions had indicated that a frequency range of 100 c to 100 kc would be necessary, it had been found that with dilute solutions the required frequency range was 400 c to 400 kc. The 500 000 ohm potentiometers were supplemented with a pair of 20 000 ohm potentiometers which facilitated setting in particular values of frequency at the high frequency end. The manipulation of the two sets of potentiometers will be explained later when the operating procedure is discussed in detail.

Construction of Oscillator. Although it has not been mentioned thus far, the most difficult problem in the development of this apparatus was that of achieving adequate frequency stability. In some respects it is also the most troublesome problem remaining. The earliest work was carried out using a Heath Model AG-9 Audio Generator with only minor circuit modifications other than those which were necessary for the substitution of an external bridged-T network. At frequencies below about 50 kc the frequency stability of the oscillator itself was adequate, but the stability was very adversely affected by switching from one cell to the other down to a frequency of about 10 kc. A number of different electrical and mechanical switching arrangements were tried with very little success until it was concluded that the effect was due to a combination of changes in contact resistance and mechanical vibration. The switching problem was finally solved by using the tapered pins and brass lugs removed from an old Wheatstone bridge. Such an arrangement gave a very low contact resistance; the pins could be removed and replaced gently; and the positions of all the movable components of the switches were accurately reproducible.

After the problem of switching from one cell to the other was solved, it became evident that the over-all precision was being limited to a marked extent by the frequency stability of the oscillator. An attempt was made to improve the situation by modification of the existing equipment, but such extensive redesign and rebuilding were necessary that the whole oscillator and power supply were rebuilt on a new chassis.

The redesign of the circuit had the object of providing the greatest possible stability in the d-c operating voltages, adequate decoupling of the oscillator from the various possible load variations, and thermal insulation to minimize the effect of room temperature variations. The circuit in figure 4 is the end result of this effort. The metering circuit was the only part of the original AG-9 which was preserved intact.

The a-c input was taken from a line voltage stabilizer which provided  $115 \pm 1\%$  over a range of input voltages from 95 to 135. This supplied a stable filament voltage through T102 to all the vacuum tubes except V108. The filament voltage for V108 was supplied by a six volt lead cell storage battery, B101, while measurements were actually in progress. For operation while measurements were not being made V108 could be switched over to T102 by means of SW103. The third position of SW103 disconnected T101 from the line, disconnected all of the filaments from T102, and connected windings W3 and W4 of T102 in series so that they could be used to recharge the battery through D101, a full-wave bridge selenium rectifier. In the charge position SW103 also disconnected the meter from the output of the oscillator and connected it across R101 so that it would indicate the charging current. R101 was chosen to give full scale deflection of the meter when this current was one ampere. D101 was derated from 1.5 to 1.0 amperes for this use.

The plate voltages were supplied by a conventional rectifier and choke input filter (C101 was chosen to have the most effect on the waveform while having negligible effect on the voltage at the filament of V101 so that the advantages of the choke input filter were retained).

The plate voltage for V110, 500 vdc, was taken directly from the output of the filter while 450 vdc was supplied to V108 and V109 by a more or less standard electronic regulator consisting of V102-V106 and the associated circuits. The operation of this regulator appeared to be very good, although equipment of sufficient sensitivity to accurately evaluate the performance was not available.

A voltage gain of about twenty, and decoupling which was normally adequate, was obtained by the addition of a voltage amplifier V110A and cathode follower V110B.

The effect of varying room temperature was counteracted by a combination of measures. The most important one was the control of room temperature to avoid sudden changes. In addition to this all of the components of the bridged-T network except the cells were built in a well insulated box. The cells were placed in Dewar flasks, each containing about 600 ml. of water to increase the thermal inertia.

When it was operating properly, the frequency stability of this oscillator was such that a change of one or two parts in  $5 \times 10^5$  was about the most encountered during the course of a measurement at any frequency below about 250 kc. The stability appeared to improve steadily with decreasing frequency but fell off very rapidly at higher frequencies.

Counter. The measurement of frequencies in all cases depended ultimately on the use of a Type 524-A Frequency Counter manufactured by the Hewlett-Packard Company, Palo Alto, California. As the name implies, this instrument physically counts the number of times some event occurs in a given interval of time. In practice, it will count "one" everytime

the input voltage passes through some predetermined value near zero in a negative direction. It thus will count pulses, or square waves, or sine waves, or what have you. This will be seen later to have an important bearing on the measurement of frequency.

Frequency Multiplier. It was evident from the beginning that some sort of frequency multiplication would be necessary in order to achieve the desired precision. For example, if a precision of one part in  $10^4$  were desired in the measurement of a one kilocycle signal, it would be necessary to count the signal for a period of ten seconds or to multiply the signal by a factor of ten and count the resulting signal for one second. To get the same precision with a 100 c signal it would be necessary to multiply by 100 and count for one second, or multiply by ten and count for ten seconds, or count for 100 seconds.

The use of a ten second count is undesirable and any thing longer than ten seconds would be very impractical, so all of the effort was devoted to development of a system of accurate multiplication.

The frequency multiplier finally developed is shown in Figure 5 and the power supply is shown in Figure 6. The values of the components are given in Table 8, and the voltages at the tube sockets are tabulated in Table 9. The remarks made earlier in reference to Tables 6 and 7 are applicable here also. The part of the power supply shown within the dashed lines was built on the main chassis and the main chassis was connected to the power supply chassis by an eight conductor cable running into PL205. The color code and corresponding pin numbers are

TABLE 8  
Description of Components of Frequency Multiplier  
(Resistors)

Components	Description	Components	Description
R201	220K, $\frac{1}{2}$ Watt	R218	470K, $\frac{1}{2}$ Watt
R202	1.0K, $\frac{1}{2}$ Watt	R219	220K, $\frac{1}{2}$ Watt
R203	56K, $\frac{1}{2}$ Watt	R220	3.3K, $\frac{1}{2}$ Watt
R204	1.0K, $\frac{1}{2}$ Watt	R221	220K, $\frac{1}{2}$ Watt
R205	100K, 2 Watt	R222	50K Potentiometer, Ohmite Type CU
R206	100K, $\frac{1}{2}$ Watt	R223	1.0M, $\frac{1}{4}$ Watt
R207	10K, $\frac{1}{2}$ Watt	R224	3.3K, $\frac{1}{2}$ Watt
R208	47K, $\frac{1}{2}$ Watt*	R225	39K, 1 Watt
R209	47K, $\frac{1}{2}$ Watt*	R226	22K, $\frac{1}{2}$ Watt
R210	220K, $\frac{1}{2}$ Watt	R227	47K, $\frac{1}{2}$ Watt*
R211	18K, $\frac{1}{2}$ Watt	R228	47K, $\frac{1}{2}$ Watt*
R212	470, $\frac{1}{2}$ Watt	R229	470K, $\frac{1}{2}$ Watt
R213	47K, $\frac{1}{2}$ Watt	R230	68K, $\frac{1}{2}$ Watt
R214	22K, $\frac{1}{2}$ Watt	R231	560, $\frac{1}{2}$ Watt
R215	47K, $\frac{1}{2}$ Watt	R232	150K, $\frac{1}{2}$ Watt
R216	47K, $\frac{1}{4}$ Watt	R233	220K, $\frac{1}{2}$ Watt
R217	22K, $\frac{1}{2}$ Watt	R234	47K, $\frac{1}{2}$ Watt*

\*Denotes matched pairs.

TABLE 8 (Cont.)

Description of Components of Frequency Multiplier  
(Resistors)

Components	Description	Components	Description
R235	47K, $\frac{1}{2}$ Watt*	R252	15K, $\frac{1}{4}$ Watt
R236	470K, $\frac{1}{2}$ Watt	R253	270K, $\frac{1}{2}$ Watt
R237	68K, $\frac{1}{2}$ Watt	R254	270K, $\frac{1}{2}$ Watt
R238	330, $\frac{1}{2}$ Watt	R255	50K Potentiometer, Ohmite Type CU
R239	220K, $\frac{1}{2}$ Watt	R256	1.0M, $\frac{1}{2}$ Watt
R240	220K, $\frac{1}{2}$ Watt	R257	5.6K, $\frac{1}{2}$ Watt
R241	47K, $\frac{1}{2}$ Watt*	R258	39K, $\frac{1}{2}$ Watt
R242	47K, $\frac{1}{2}$ Watt*	R259	22K, $\frac{1}{2}$ Watt
R243	470K, $\frac{1}{2}$ Watt	R260	47K, $\frac{1}{2}$ Watt*
R244	56K, $\frac{1}{2}$ Watt	R261	47K, $\frac{1}{2}$ Watt*
R245	330, $\frac{1}{2}$ Watt	R262	470K, $\frac{1}{2}$ Watt
R246	220K, $\frac{1}{2}$ Watt	R263	55K, $\frac{1}{2}$ Watt
R247	220K, $\frac{1}{2}$ Watt	R264	330, $\frac{1}{2}$ Watt
R248	100K, $\frac{1}{2}$ Watt*	R265	220K, $\frac{1}{2}$ Watt
R249	100K, $\frac{1}{2}$ Watt*	R266	1.0M, $\frac{1}{2}$ Watt
R250	4.7K, $\frac{1}{2}$ Watt	R267	470, $\frac{1}{2}$ Watt
R251	680K, $\frac{1}{2}$ Watt	R268	5.1K, 2 Watt

\*Denotes matched pairs.



TABLE 8 (Cont.)

Description of Components of Frequency Multiplier  
(Resistors)

Components	Description	Components	Description
R269	470, $\frac{1}{2}$ Watt	R278	30K, 2 Watt
R270	220K, $\frac{1}{2}$ Watt	R279	30K, 2 Watt
R271	8.2K, $\frac{1}{2}$ Watt	R280	2.2K, $\frac{1}{2}$ Watt
R272	100K, 1 Watt	R281	1.0K, $\frac{1}{2}$ Watt
R273	45K, 20 Watt, Wire-wound	R282	220K, $\frac{1}{2}$ Watt
R274	1.0M, $\frac{1}{2}$ Watt	R283	220K, $\frac{1}{2}$ Watt
R275	250K, $\frac{1}{2}$ Watt	R284	100K Potentiometer, Ohmite Type J
R276	100, $\frac{1}{2}$ Watt	R285	39K, 2 Watt
R277	3.0, $\frac{1}{2}$ Watt		

All values in ohms

K indicates X1000

M indicates X1000000

\*Denotes matched pairs.

TABLE 8 (Cont.)

Description of Components of Frequency Multiplier  
(Capacitors)

Component	Description	Component	Description
C201	0.02, 600 vdc	C222	0.01, 600 vdc
C202	0.005, 600 vdc	C223	1.0, 450 vdc, electrolytic
C203	0.05, 600 vdc	C224	0.01, 600 vdc
C204	0.05, 600 vdc	C225	0.003, mica
C205	0.05, 600 vdc	C226	0.01, 600 vdc
C207	0.05, 600 vdc	C227	5, 250 vdc, electrolytic
C208	1.0, 450 vdc, electrolytic	C228	0.005, 600 vdc
C209	200 uuf, mica	C229	0.003 mica
C210	30-700 uuf variable	C230	0.01, 600 vdc
C211	800 uuf, mica	C231	12, 150 vdc, electrolytic
C212	250 uuf, mica	C232	0.005, 600 vdc
C213	0.003, mica	C233	0.003, mica
C214	250 uuf, mica	C234	50 uuf, mica
C215	250 uuf, mica	C235	1.0, 450 vdc, electrolytic
C217	1.0, 450 vdc, electrolytic	C236	10 uuf, ceramic
C218	0.003, mica	C237	25 uuf, ceramic
C219	0.005, 600 vdc	C238	50 uuf, mica
C220	1.0, 450 vdc, electrolytic	C239	100 uuf, ceramic
C221	0.01, 600 vdc	C240	100 uuf, ceramic

TABLE 8 (Cont.)

Description of Components of Frequency Multiplier  
(Capacitors)

Component	Description	Component	Description
C241	300 uuf, mica	C252	5, non-polarized electrolytic
C242	1000 uuf, mica	C253	0.005, 600 vdc
C243	0.5, 200 vdc, paper	C254	0.05, 600 vdc
C244	0.003, mica	C255	40, 450 vdc, electrolytic
C245	0.001, 600 vdc	C256	40, 450 vdc, electrolytic
C246	0.01, 600 vdc	C257	1.0, 200 vdc, paper
C247	0.02, 600 vdc	C258	0.1, 600 vdc
C248	0.002, 600 vdc	C259	1.0, 450 vdc, electrolytic
C249	0.1, 600 vdc	C260	20, 450 vdc, electrolytic
C250	0.003, mica	C261	20, 450 vdc, electrolytic
C251	0.003, mica		

All capacitances are in microfarads, unless otherwise indicated.

TABLE 8 (Cont.)

Description of Components of Frequency Multiplier  
(Miscellaneous)

Component	Description
PL201	Shielded "Mike" connector, signal input
PL202	Shielded "Mike" connector, signal out to frequency counter
PL203	Shielded "Mike" connector, signal out to scope
PL204	Fused plug, includes F201 and F202
PL205	Cinch-Jones, series 300, 15 contact, plug and socket
RY201	DPST phone type relay, 6 volt coil, shown in energized position
RY202	DPST 115 vac relay, shown in energized position
F201	1 amp Slo-Blo fuse, type 3AG or equivalent
F202	1 amp Slo-Blo fuse, type 3AG or equivalent
SW201	Wafer switch, 1 pole, 10 pos, progressively shorting; as shown on schematic, positions are brought in from left to right with ccw rotation
SW202	Wafer switch, 1 pole, 10 pos, progressively shorting; as shown on schematic, positions are brought in from left to right with ccw rotation
SW203	Wafer switch, 4 poles, 2 pos, shown in pos 1 on schematic

TABLE 8 (Cont.)

Description of Components of Frequency Multiplier  
(Miscellaneous)

Component	Description
SW204	Wafer switch, 1 pole, 11 pos, shown in pos 5 on schematic
SW205	SPST toggle switch, shown in "power on" position
L201	RF choke with powdered iron core added, natural frequency about 18 kc
L202	RF choke with powdered iron core added, natural frequency about 350 kc
L203	Filter choke, 12 H. at 80 mac
CR201-CR216	Crystal diodes, Sylvania type IN34A or equivalent
V201	Medium-mu twin triode, type 5963
V202-V203	Sharp cut-off pentode, type 6AK5
V204	Medium-mu triode, type 6C4
V205-V208	Sharp cut-off pentode, type 6AK5
V209	Medium-mu triode, type 6C4
V210	Sharp cut-off pentode, type 6AK5
V211	Medium-mu twin triode, type 5963
V212	Medium-mu triode, type 6C4
V213	Gas regulator, type OB2

TABLE 8 (Cont.)

Description of Components of Frequency Multiplier  
(Miscellaneous)

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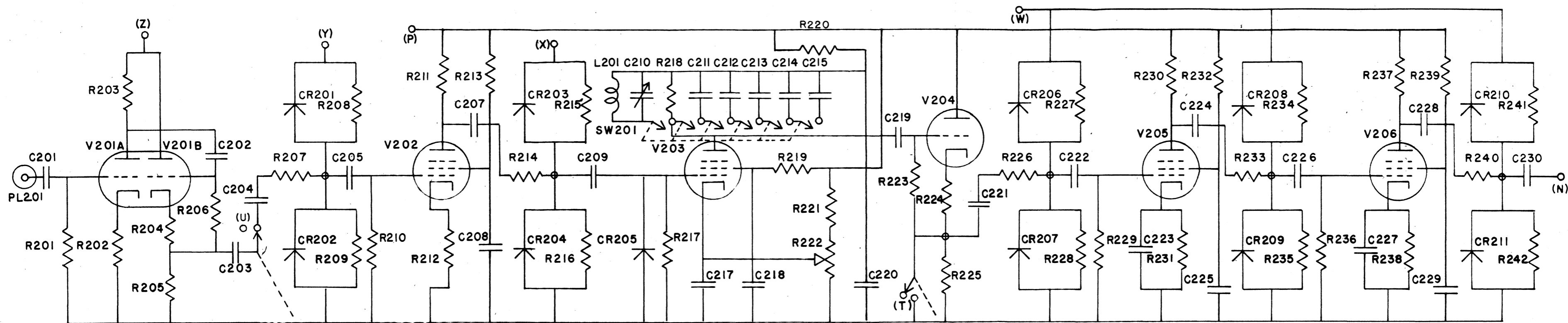
Component	Description
V214	Sharp cut-off pentode, type 6AU6
V215	Low-mu twin triode, type 6BX7
V216	Full-wave vacuum rectifier, type 6X4
T201	Plate transformer rated at about 860 vet 100 ma
T202	Filament transformer, rated at 6.3 v at 11 a

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TABLE 9  
 Voltages at Vacuum Tube Sockets  
 in Frequency Multiplier

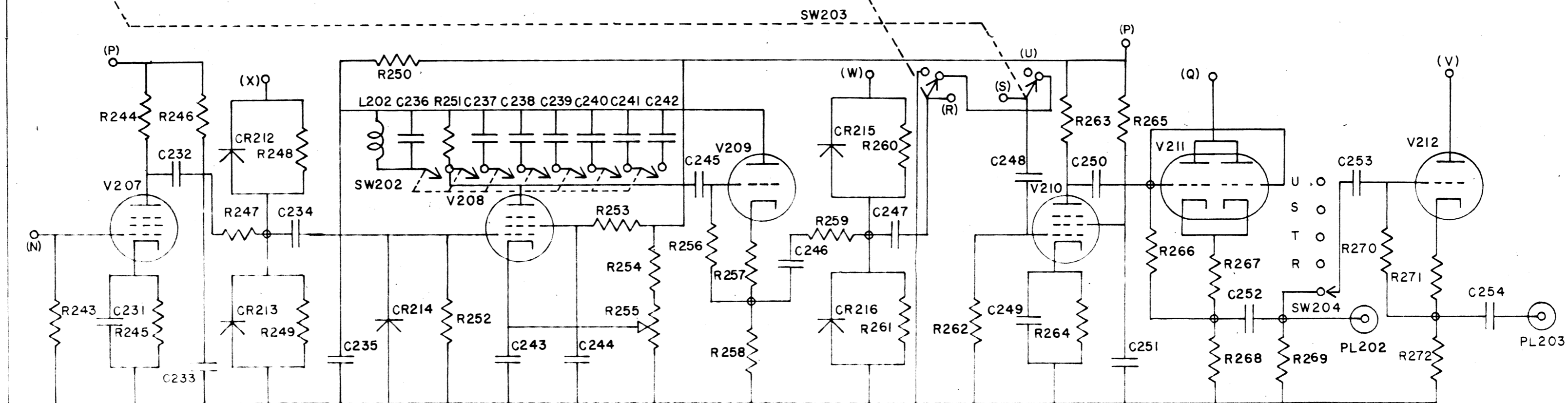
Tube	Pin 1	Pin 2	Pin 3	Pin 4	Pin 5	Pin 6	Pin 7	Pin 8	Pin 9
V201	80	0	2.5	H*	H	190	65	68	H
V202	0	3.0	H	H	144	130	3.0		
V203	0	55	H	H	215	220	55		
V204	230	IC	H	H	230	50	90		
V205	0	1.4	H	H	102	112	1.4		
V206	0	1.3	H	H	44	74	1.3		
V207	0	1.1	H	H	86	56	1.1		
V208	0	40	H	H	200	220	40		
V209	230	IC	H	H	230	28	56		
V210	0	1.0	H	H	100	90	1.0		
V211	300	49	86	H	H	300	49	86	H
V212	300	IC	H	H	300	90	110		
V213	107	0	IC	0	107	IC	0		
V214	102	107	H	H	220	68	107		
V215	220	340	230	220	340	230	4	H	
V216	340ac	NC	H	H	NC	340ac	340		

\*Heaters biased at 80 vdc  
 Conditions:  
 No input  
 No external load  
 R222 and R255 full ccw  
 SW 203 in pos 1  
 SW 204 in pos 4  
 L201 and L202 switched in



- (P) + 250 VDC (REGULATED)
- (Q) + 330 VDC (UNREGULATED)
- (V) + 340 VDC (UNREGULATED)
- (W) + 0.2 VDC (BATTERY)
- (X) + 6.0 VDC (BATTERY)
- (Y) + 2.0 VDC (BATTERY)
- (Z) + 210 VDC (UNREGULATED)
- SW203 SHOWN IN POSITION 1
- SW204 SHOWN IN POSITION 5

FIGURE 5  
SCHEMATIC OF FREQUENCY  
MULTIPLIER





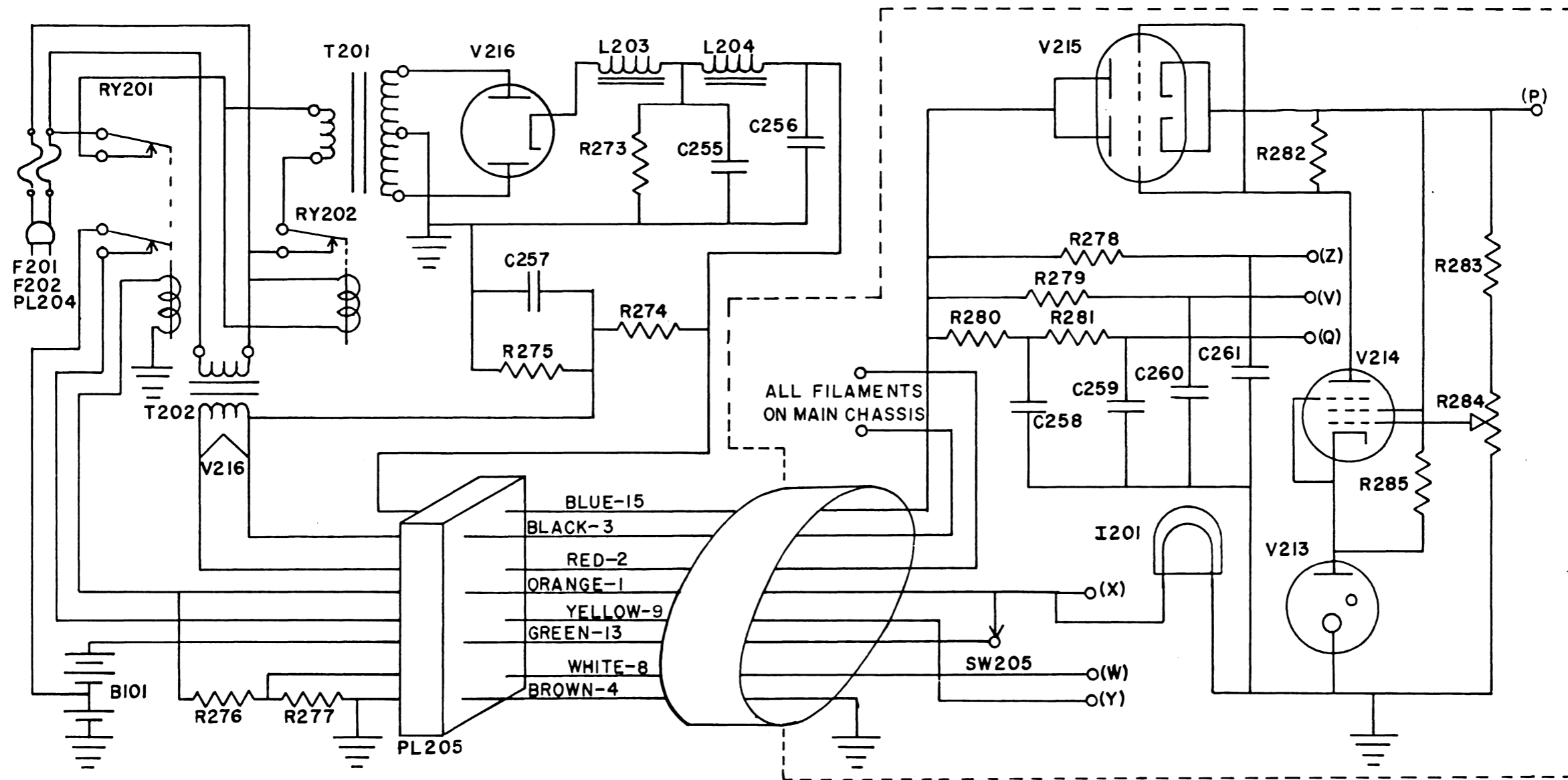


FIGURE 6

SCHMATIC OF FREQUENCY  
MULTIPLIER POWER SUPPLY

given in Figure 5. The only unconventional aspect of the entire power supply was the use of relays to turn on the 2 vdc from B101 and to connect the primary of the plate transformer to the line. This made it unnecessary to bring the line voltage into the main chassis.

Multiplication was achieved by means of two cascaded ringing oscillators. The input signal was amplified by V201A and the cathode follower, V201B, served to decouple the following circuits from the input. The wave was clipped, amplified by V202, clipped again, differentiated by C209 and R217, and the negative pulses removed by CR205. The resulting series of positive pulses were applied to the grid of V203 which was normally biased past cut-off by adjusting R222. The sudden pulse of current caused by a positive pulse on the grid of V203 had to pass through the tuned circuit formed by L201 and whatever capacitors were in parallel with it. The abrupt cessation of this current caused by the return of V203 to the non-conducting state caused the tuned circuit to oscillate, or ring, at a frequency determined by the circuit parameters. The capacitance was adjusted so that this frequency was an even multiple of the repetition rate of the pulses which in turn was the same as the input frequency. If the pulse repetition rate were then great enough that the oscillations were not completely damped between pulses, the ringing oscillator would lock in with the pulses. The frequency out of the stage would then be an exact, constant, multiple of the input frequency. This stage worked into a cathode follower because the high input impedance prevented undue damping of the tuned circuit. R218 was incorporated to allow frequencies higher

than the natural frequency of L201 to pass through the stage.

This whole process was repeated again in the next five stages. Several stages of clippers were necessary to obtain adequate square waves which would give sharp pulses after differentiation. (It would probably be possible to accomplish the same thing with fewer stages by more careful design since most of this was done on a pure "cut and try" basis.) Symmetry in the group of pulses going into V208 is rather important and had to be obtained by carefully tuning the previous multiplier. If this were not done, the time between the pulses would vary periodically and difficulty was encountered in getting the second multiplier to lock in properly.

SW203 permitted a signal to be passed through without multiplication so that the output frequency of the oscillator could always be set without ambiguity, and signals having frequencies greater than the natural frequency of L202 could be passed through. V211 provided a low impedance output to the frequency counter through PL202 while an oscilloscope could be connected to PL203 and the waveform at various points in the multiplier examined by proper positioning of SW204. Cathode follower V212 prevented loading of the circuits being examined.

This scheme usually worked quite well. The combination of two multipliers in this manner permitted the one second count to be used down to about 1.0 kc which was usually as low as it was necessary to go.

Cells. The cells used in this investigation were made by J. C. Balsbaugh. The plates were concentric nickel cylinders which were supported in a large test tube by a Teflon cap. The conductors, which penetrated the cap, did not fit tightly enough to give an air tight seal, nor was the fit of the cap in the test tube a good one. In order to prevent absorption of atmospheric water vapor, the tops of the Teflon caps were given a heavy coating of polystyrene and the test tubes were fitted with thin rubber tubes which sealed against the test tube and against the Teflon cap when it was inserted into the test tube. This arrangement gave satisfactory results.

The capacitances of the empty cells were measured at one kilocycle by connecting them directly (no leads involved) to the terminals of a General Radio 716-C Capacitance Bridge. The measured capacitance of Cell I was 114.2 uuf while that of Cell II was 108.2 uuf.

Detailed Operating Procedure. Solutions of cellulose acetate in dioxane were prepared by drying the polymer at 105° for about one hour, allowing it to cool in a desiccator and then weighing by difference enough to give the desired concentration when dissolved in 65 ml. of dioxane. The cellulose acetate was placed in a bottle having a screw cap, 65 ml. of dioxane were then pipetted into the bottle and the cap was quickly screwed into place to prevent absorption of moisture from the atmosphere. The bottle was then placed on a mechanical shaker and shaken until all of the solid material which would dissolve had dissolved. Some samples contained appreciable quantities of foreign matter. After

the last of the polymer had disappeared, the solution was allowed to stand for at least 24 hours before any measurements were attempted.

When it was desired to make a run on the solution, the rubber gland was placed on the test tube, all of the solution was added through a funnel, and then the cell was quickly slipped into place and a seal made. The solvent was treated in the same way as the solution. The solution usually was placed in Cell II and the solvent in Cell I, because the dielectric constant of the solution was usually slightly higher than that of the solvent. This meant that the capacitances of the filled cells were slightly closer together than they would have been otherwise. This was desirable because it meant less movement of  $C_p$  during a run.

The cells were allowed to remain at 25° for a few hours in order to come to temperature equilibrium and then they were placed in Dewar flasks. The Dewars and the cells were fixed fairly rigidly in position on a wood base by means of copper rods. One end of each rod had a banana plug to fit the cell and the other end was made to be tightly bolted to one of the rods which held the outer lugs of SW104 and SW105 in place. The whole assembly comprised of SW104, SW105, the Dewars, and the cells containing solution and solvent was then bolted down in its place in the oscillator. Electrical connections were made by fitting the ends of the brass rods, which held the inner lugs of SW104 and SW105 in place, with banana plugs. These banana plugs mated with copper tubes which connected into the bridged-T network in series with  $C_p$ .

For convenience, the ganged 500 000 ohm potentiometers, R123 and R126, will be referred to collectively as R' and the ganged 20 000 ohm potentiometers, R124 and R125, will be referred to as R" in the following discussion. It should be mentioned at this point that R" did not have mechanical stops, so that it was possible for it to be in a position where the wiper did not contact the winding.

If the battery had just been charged, the oscillator was warmed up with SW103 in position 3, otherwise SW103 was placed in position 2 and SW101 was turned on. While the filaments were warming up, SW104 and SW105 were positioned so that both cells were disconnected; the oscillator control, R122, was turned to the full counter-clockwise, ccw, position; the output level control, R130, was placed in the full clockwise, cw, position; Cp was set to 1150.0 uuf; R' was placed in the full ccw position, if there was any doubt concerning the position of R"; and then, the filaments having warmed up, SW102 was turned on.

A certain amount of care had to be exercised in turning on the frequency multiplier, because it was possible for R222 and SW201 or R255 and SW202 to be in such positions that there was essentially no load in the plate circuit of the corresponding vacuum tube, the d-c resistance of the inductors being low, and the grid bias was effectively removed. If the B<sup>+</sup> were turned on under such conditions, the tubes would be ruined in a few minutes. If there were no uncertainty in this respect, the B<sup>+</sup> could be turned on by means of SW205 without further ado. If there were any doubt concerning the positions of the controls however, R222 was set to the full ccw position which biased the tube well

past cut-off. R255 was positioned similarly. The selector switch, SW204, was placed in position 5, the position shown in the circuit diagram; and SW203, which is shown in position 1 in the schematic, was placed in position 2 so that both multipliers were bypassed.

The cell containing solvent was then switched into the circuit by placing the tapered pins in the proper holes of SW104 and SW105 and the oscilloscope checked to make sure that there was no signal coming out of the multiplier. If there were a signal indicated, its source had to be determined and eliminated. When this had been done, the oscillator control, R122, was advanced slowly until there was an indication of about 1.0 on the ten scale of the meter or until the potentiometer had been moved through  $1/2$  to  $1/3$  of its total travel. If it could be moved that far with no indication on either the oscilloscope or the meter, R" was probably in a position where the wiper did not contact the winding. This situation could be corrected by moving the knob controlling R" two full turns in either direction. This would move the wiper far enough through the reducing drive to get it off the "Dead spot". A few seconds after moving R" in this manner, the meter and the oscilloscope both would indicate that the oscillator was operating; and, after the signal had stabilized, the counter would indicate a frequency less than one kilocycle. R122 could then be readjusted to give a reading of about one on the meter. In order to make the final adjustment of R122, R' was moved to the full cw position, R" adjusted to give an output signal of 10.00 kc, R' moved ccw to give a frequency of 3.0 kc and R122 adjusted so that the meter read exactly 3.0 on the ten scale.

If everything was satisfactory at this point the oscillator was then checked for stability by turning R' to the full cw position and adjusting R'' to the highest frequency that was desired in the particular run. (It is assumed in the following discussion that this frequency was greater than 100 kc.). The oscillator could then be checked for frequency stability by observing the counter over a period of a few minutes. A slow steady drift of as much as two or three per minute in the sixth significant figure could be tolerated, but erratic readings could not. If the stability were not satisfactory, the cell was unplugged and the stability rechecked periodically by plugging the cell back in until it was found to be satisfactory.

After the frequency had stabilized, measurements were begun to determine whether the difference between the solvent and solution was constant at constant frequency. This was done by plugging in Cell II (solution) and setting Cp to 1150.0 uuf by approaching this value from above. The frequency was then read exactly. Cell II was then unplugged and Cell I (solvent) plugged in and Cp adjusted to Cp I, the value of Cp at which the frequency was the same as it was with Cell II in. Cell II was plugged in again, Cp read, and reset to 1150.0 uuf in order to insure that no significant change in frequency had taken place during the measurement. Cell II was then switched out and everything left undisturbed for about an hour whereupon the measurement was repeated. This was repeated until the change in the value of Cp I became less than 0.5 uuf per hour. The battery had to be used judiciously while stability was being attained to prevent discharging it prematurely.



The final setting of  $C_p$  always had to be approached from the same direction in order to obtain reproducible results. This requirement could not be attributed to backlash in the driving mechanism of the capacitor since it was much larger in magnitude than the mechanical backlash. It seemed that once the oscillator had stabilized at a particular frequency there was a slight tendency for the frequency to remain unchanged with small, slow variations in  $C_p$  about a fixed value. If  $C_p$  were moved slowly and continuously in one direction there seemed to be a tendency for the frequency to change in a more or less stepwise manner. Aside from this the behavior was very similar in all respects to that which would be expected from mechanical backlash, so it was treated in exactly the same way.

After everything had stabilized, the run could be made by setting the desired frequency with  $R''$  down to 10.00 kc and with  $R'$  below 10.00 kc and making a measurement at each frequency in exactly the same way that they were made during the check for stabilization. It was found to be desirable to go back and repeat the measurement at the highest frequency after the determination at the lowest frequency was complete, in order to determine how much of the change was due to dispersion and how much should simply be attributed to variations in the capacitances of the cells as a function of time. The latter effect was usually negligible if everything had reached equilibrium before the run was begun.

Operation of the Frequency Multiplier. Signals of frequency greater than about 320 kc could not be passed through the multiplier

satisfactorily, so the multipliers had to be bypassed by placing SW203 in position 2. At 320 kc or lower the signal was passed through both multipliers even though signals of frequency greater than 158 kc were not actually multiplied. In order for signals to pass through the multiplier satisfactorily, it was necessary to properly adjust R222 and R225. The procedure used was to set SW202 so that L202 and C236 were in parallel with R251. R255 was then moved in a cw direction (with a signal input of about 300kc) to a position where the gain, as indicated by the trace on the oscilloscope, failed to increase with further rotation. The control was then set between this point and the minimum usable signal. R222 was then moved in a cw direction until the gain just started to increase.

The resonant frequency of L202 and C236 was about 300 kc, so as the frequency was reduced, capacitance had to be switched in. When the frequency was down to 158 kc all the capacitors except C236 could be switched out in order to double the 158 kc signal. The procedure that was used from this point on is practically impossible to describe except in very general terms, because it varied from time to time, from one frequency to another, and required a lot of manipulation of the controls. The object, however, was always to obtain a waveform at the output which was symmetrical and which did not have any partially complete cycles. An indication of a satisfactory waveform could be obtained from the oscilloscope, but the final criterion was always a stable count on the frequency counter. For example, the output voltage, as indicated on the oscilloscope might be observed

to go through four complete cycles. Then, halfway through the fifth cycle where the voltage was approaching zero with a negative slope, it might be reversed by the occurrence of the pulse at the grid of V208. A spike would be formed which could vary markedly in height as a result of a small change in the time between the pulses or the duration of the pulses. It can be seen that if the point at which the counter does, or does not, count "one" lies within the range of this variation, the count will be erratic. The obvious remedy is to change the frequency of the tuned circuit so that the voltage is approaching its maximum positive value as the pulse occurs.

This behavior is particularly noticeable at the lower frequencies where high multiplication factors must be obtained in the first stage. The comparatively long trains of pulses at the grid of V208, which result from single pulses at the grid of V203, show marked variation in size and shape within a given train. At these frequencies the difficulty had to be overcome by tuning both resonant circuits and by cautious adjustment of R222 and R255.

It was usually possible to keep an output of about 300 kc until the input frequency was down to about 39.8 kc. By the time the input frequency was down to 10 kc, it usually had been necessary to reduce the output to about 200 kc. The first multiplier stage was most often brought into action at 10 kc and the resonant frequencies of both ringing oscillators had to be decreased as the input frequency was decreased further. It was frequently possible to get multiplication up to 160 kc with an input of 1.26 kc. Multiplication of 1.00 kc to 160 kc was

difficult, but it was relatively easy to get 125 kc. Multiplication of 0.795 kc to 125 kc was exceedingly difficult and the adjustments necessary to accomplish it were time consuming. The ten second count had to be used for frequencies below 0.795 kc.

There was one inherent drawback to this method that took on particular importance at the lower frequencies. As the input frequency was varied over a wide range, the output of the multiplier varied with it within certain limits and then the multiplication factor changed. When the frequency fed into the multiplier became so low that the change in frequency at the output of the multiplier (which occurred as a result of changing from CxI to CxII with a fixed value of Cp in the oscillator) was greater than the frequency fed into the multiplier, a certain amount of ambiguity existed in the determination of the second setting of Cp.

There are two ways in which this uncertainty can be circumvented, however. One idea, which occurred when the difficulty was first anticipated during construction, was the obvious one of decreasing the multiplication factor. This was used successfully for a time. It consisted merely of making an initial approximate setting of Cp using a low factor and then increasing the multiplication factor and the sensitivity so that a more precise setting of Cp could be made. The other method, which was used almost exclusively, was to begin each run at the high end of the frequency spectrum where there was no ambiguity. When the range where there was an ambiguity was reached, the approximate position of the second setting of Cp was known from the previous

readings. In practice,  $C_p$  was set to within one or two micro-microfarads of the previous reading at all frequencies in order to save time; therefore, the problem was eliminated without additional manipulation.

Occasionally some difficulty was encountered which was caused by the main oscillator being pulled by one of the ringing oscillators, but this was usually readily eliminated by changing the frequency of the ringing oscillator and working on another multiple of the input frequency.

Testing the Apparatus. There was no reliable standard against which this apparatus could be calibrated directly. It was thus necessary to build into it a higher standard of performance than might have otherwise been required.

Preliminary testing was carried out using empty cells, it being assumed that there should be no observable change in the difference between the capacitances of the cells over the frequency range. The runs using empty cells were carried out according to the procedure given earlier except that  $C_p$  was set to 600.0 uuf and the lowest frequency which could be reached with  $R''$  was 20.00 kc instead of 10.00 kc. In the first such run to give encouraging results an apparent change of only 0.02 uuf was found in going from 250 kc to 20 kc, but an apparent change of 0.10 uuf was found in going from 20.0 kc to 1.00 kc. It was determined later that most of this was due to the use of water in the Dewars in an attempt to increase the thermal inertia and thus to decrease temperature effects.

The results of a later run without water in the Dewars are given in Table 10. It will be noted that the apparent change in the difference between the capacitances of the two cells was 0.01 uuf when the frequency was changed directly from 393 kc to 1.58 kc. (These are the first two values given in the table.) When the frequency change was spread over a period of time, however, there was an apparent change of 0.08 uuf observed over the same frequency range. The apparatus was in a constant temperature room at this time and this slow change was found to be due to small long term temperature changes in the room. In order to test this and to further the testing of the apparatus, both cells were filled with solvent and another run was made. Some minor changes had been made in the meantime to increase the thermal insulation around the cells and to prevent slow changes in the room temperature. The results of this run are given in Table 11. These were felt to be very satisfactory. Conclusions based on some of the earlier work had to be thrown out on account of these innovations. It was found that although the critical frequencies were the same, the shapes of the dispersion curves for some of the fractions were altered somewhat.

TABLE 10  
Results of Testing Apparatus  
Empty Cell vs. Empty Cell

F(kc)	C <sub>xII</sub> (uuf)
393.	108.95
1.58	108.94
2.50	108.93
3.98	108.93
6.32	108.90
10.0	108.90
15.8	108.90
25.8	108.90
39.7	108.89
63.1	108.88
100.	108.88
158.	108.87
250.	108.87
393.	108.86

TABLE 11  
Results of Testing Apparatus  
Solvent vs. Solvent

F(kc)	C <sub>x</sub> II
398.0	237.85
1.26	237.83
2.00	237.83
3.16	237.83
5.01	237.83
7.92	237.83
12.6	237.83
20.0	237.82
31.6	237.82
50.1	237.81
79.3	237.81
127.	237.80
200.	237.80



## DISPERSION MEASUREMENTS

Two general classifications of measurements must be considered here; namely, those made before and after the final refinement of the technique. The difference in results obtained before and after is slight, but it appears to be significant, so the distinction should be made. Results of runs on fraction 12E offer a good illustration. The data obtained before and after the final refinement are summarized in Table 12. Both sets of data are plotted in Figure 7 where it can be seen that the points where  $\log f$  is 3.8 and 4.0 are off. If the circled points were considered alone, however, it could easily be concluded that the point where  $\log f$  is 3.6 was the bad one.

It had been found earlier in an investigation of ethyl cellulose that the dispersion curve was altered markedly by heating the solution for several hours before making the measurement (72) This possibility was checked for the cellulose acetate-dioxane system, and it was found that heating the solution had negligible effect on the dispersion.

In some cases there appeared to be a tendency for the capacitance to hit a maximum rather than to become constant at the low frequency end of the dispersion region. The cause of this was not apparent. In cases where this behavior was noticed, the capacitance at the maximum point was taken as the low frequency value.

Some fractions were run at two different concentrations in order to determine how much influence the concentration had on the critical frequency and the dispersion curve. In the case of fraction 12B, the

TABLE 12  
 Results of Dispersion Measurements  
 On Fraction 12E

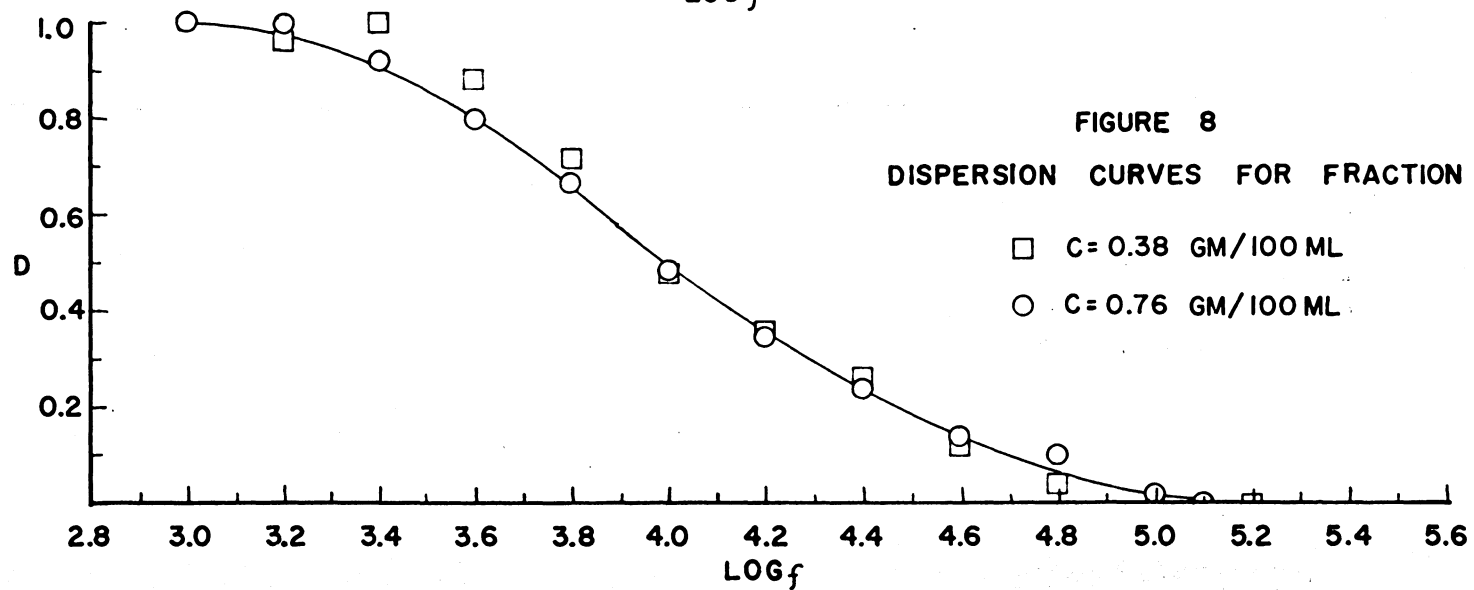
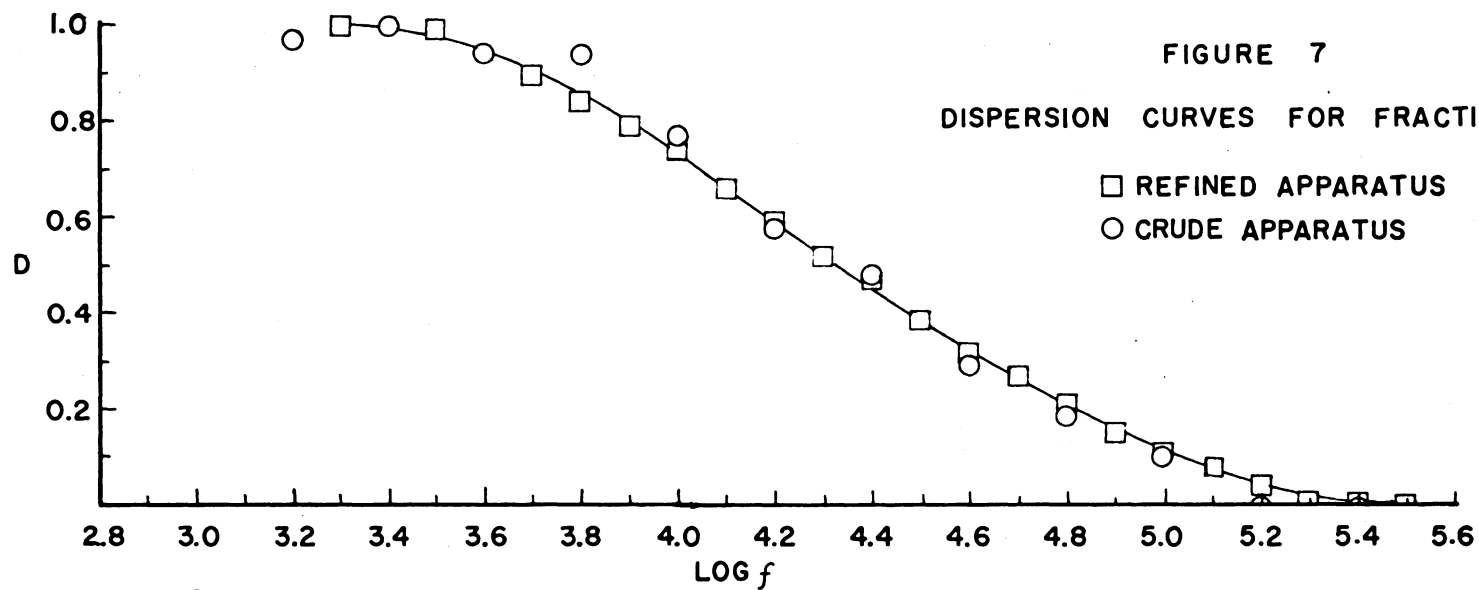
F(kc)	Before Refinement of Measurement 0.63 gm./100 ml.		After Refinement of Measurement 0.54 gm./100 ml.	
	C <sub>xI</sub>	D	C <sub>xII</sub>	D
316.			235.65	
1.26			236.13	1.02
1.58	240.15	0.97	236.14	1.04
2.00			236.12	1.00
2.51	240.16	1.00	236.12	1.00
3.15			236.12	1.00
3.98	240.14	0.94	236.09	0.94
5.02			236.08	0.92
6.31	240.14	0.94	236.05	0.86
7.96			236.02	0.80
10.0	240.09	0.77	235.99	0.74
12.6			235.95	0.66
15.8	240.03	0.58	235.92	0.60
20.0			235.88	0.52
25.1	240.00	0.48	235.85	0.46
31.6			235.82	0.40
39.8	239.94	0.29	235.78	0.32
50.2			235.75	0.26

TABLE 12 (Cont.)

Results of Dispersion Measurements

On Fraction 12E

F(kc)	Before Refinement of Measurement 0.63 gm./100 ml.		After Refinement of Measurement 0.54 gm./100 ml.	
	C <sub>XI</sub>	D	C <sub>XII</sub>	D
63.1	239.91	0.19	235.73	0.22
79.3			235.70	0.16
100.	239.88	0.10	235.68	0.12
126.			235.67	0.10
158.	239.85	0.00	235.64	0.04
200.			235.63	0.02
251.	239.85	0.00	235.62	0.00
316.			235.62	0.00



results were typical, and changing the concentration from 0.76 to 0.38 gm./100 ml. had no effect on the critical frequency, although there was some distortion of the dispersion curve. The results for the two concentrations are given in Table 13 and plotted in Figure 8.

The relationship between the critical frequency and intrinsic viscosity was of interest, so the dielectric dispersion curves of several fractions were determined in order to find their critical frequencies in dilute solutions. The calculated capacitances of the cell containing solution are given in Table 14. The fractions marked with asterisks in this table are those which were run in the earlier stages of the investigation. The apparatus was somewhat more refined for the other fractions and the blends. At the outset of the investigation, it was hoped that a relationship might be found between the dielectric dispersion curve and the molecular weight distribution curves. In order to investigate this possibility, dispersion curves were determined for the original material and three artificial blends. The results of these measurements are given in Tables 15 and 16.

TABLE 13  
 Results of Dispersion Measurements  
 On Fraction 12B

f(kc)	0.38 gm./100 ml.		0.76 gm./100 ml.	
	C <sub>x</sub>	D	C <sub>x</sub>	D
1.00			233.12	1.00
1.58	247.17	0.96	233.12	1.00
2.51	247.18	1.00	233.08	0.92
3.98	247.15	0.88	233.02	0.80
6.31	247.11	0.72	232.95	0.67
10.0	247.05	0.48	232.86	0.49
15.8	247.02	0.36	232.79	0.35
25.1	246.97	0.16	232.73	0.24
39.8	246.96	0.12	232.68	0.14
63.1	246.94	0.04	232.66	0.10
100.	246.93	0.00	232.62	0.02
158.	246.92	0.00	232.61	0.00
200.			232.61	0.00
251.	246.93	0.00		
316.	246.93	0.00		

TABLE 14

Summary of Capacitance Data for Fractions

Fraction Conc. f(kc)	21A* 0.46 gm./100ml.	31C* 0.51 gm./100ml.	31B* 0.50 gm./100ml.
0.631			237.19
0.795	235.80		
1.00	235.81		237.19
1.58	235.80		237.17
2.51	235.76	235.16	237.15
3.98	235.70	235.16	237.11
6.31	235.65	235.15	237.07
10.0	235.59	235.12	237.04
15.8	235.55	235.09	236.98
25.1	235.53	235.05	236.94
39.8	235.49	235.00	236.91
63.1	235.47	234.93	236.88
100.	235.47	234.92	236.87
158.		234.87	236.87
251.		234.87	

TABLE 14 (Cont.)

Summary of Capacitance Data for Fractions

Fraction	42C	A	41C	43B
f(kc)	0.59 gm./100ml.	0.59 gm./100ml.	0.61 gm./100ml.	0.61 gm./100ml.
0.795		244.54		
1.00	244.43	244.54		
1.26	244.42	244.52		
1.58	244.41	244.52		
2.00	244.40	244.50		
2.51	244.29	244.46	248.81	
3.16	244.37	244.43	248.82	
3.98	244.34	244.39	248.82	
5.02	244.32	244.36	248.82	
6.31	244.30	244.31	248.80	252.54
7.95	244.25	244.27	248.79	
10.0	244.21	244.22	248.76	252.54
12.6	244.19	244.18	248.74	252.51
15.8	244.14	244.13	248.72	252.48
20.0	244.10	244.09	248.69	252.47
25.1	244.06	244.04	248.66	252.44
31.6	244.02	244.01	248.63	252.42
39.8	243.99	243.98	248.60	252.39
50.2	243.96	243.94	248.57	252.36
63.1	243.93	243.91	248.54	252.33



TABLE 14 (Cont.)

Summary of Capacitance Data for Fractions

Fraction	42C 0.59 gm./100ml.	A 0.59 gm./100ml.	41C 0.61 gm./100ml.	43B 0.61 gm./100ml.
79.5	243.89	243.88	248.52	252.30
100.		243.86	248.48	252.28
126.	243.85	243.84	248.46	
158.		243.83	248.45	252.24
200.	243.83	243.81	248.43	252.21
251.		243.78	248.42	252.19
316.	243.82	243.77	248.41	252.18
398.		243.77	248.40	252.17

TABLE 15  
Summary of Capacitance and Dispersion Data  
for the Original Material  
0.45 gm./100 ml.

$f(\text{kc})$	$C_x$	D
1.58	232.37	1.00
2.51	232.36	0.96
3.98	232.35	0.93
6.31	232.32	0.82
10.0	232.28	0.68
15.8	232.26	0.61
25.1	232.21	0.43
39.8	232.18	0.32
63.1	232.14	0.18
100.	232.12	0.11
158.	232.10	0.04
251.	232.09	0.00
398.	232.09	0.00

TABLE 16

Summary of Capacitance and Dispersion Data  
for Blends

f(kc)	Blend I		Blend II		Blend III	
	0.59 gm./100 ml. C <sub>x</sub>	D	0.59 gm./100 ml. C <sub>x</sub>	D	0.59 gm./100 ml. C <sub>x</sub>	D
1.58			234.19	1.02		
2.00	249.99	1.00	234.18	1.00		
2.51	249.99	1.00	234.18	1.00	230.46	0.98
3.16	249.99	1.00	234.17	0.98	240.47	1.00
3.98	249.99	1.00	234.16	0.96	240.47	1.00
5.02	249.98	0.98	234.15	0.93	240.46	0.98
6.31	249.94	0.89	234.13	0.89	240.45	0.95
7.95	249.92	0.85	234.10	0.82	240.43	0.91
10.0	249.89	0.78	234.08	0.78	240.41	0.86
12.6	249.86	0.72	234.06	0.73	240.38	0.79
15.8	249.84	0.67	234.02	0.64	240.37	0.77
20.0	249.81	0.61	233.98	0.56	240.33	0.67
25.1	249.78	0.54	233.96	0.51	240.29	0.58
31.6	249.75	0.48	233.93	0.44	240.27	0.53
39.8	249.71	0.39	233.90	0.38	240.23	0.44

TABLE 15 (Cont.)

Summary of Capacitance and Dispersion Data  
for Blends

f(kc)	Blend I 0.59 gm./100 ml.		Blend II 0.59 gm./100 ml.		Blend III 0.59 gm./100 ml.	
	C <sub>x</sub>	D	C <sub>x</sub>	D	C <sub>x</sub>	D
50.2	249.68	0.33	233.87	0.31	240.21	0.40
63.1	249.65	0.26	233.84	0.24	240.19	0.35
79.5	249.63	0.22	233.83	0.22	240.15	0.26
100.	249.60	0.15	233.79	0.13	240.13	0.21
126.	249.59	0.13	233.77	0.09	240.10	0.14
158.	249.56	0.07	233.75	0.04	240.09	0.12
200.	249.54	0.02	233.75	0.04	240.07	0.07
251.	249.53	0.00	233.74	0.02	240.05	0.02
316.	249.52	0.00	233.73	0.00	240.04	0.00
398.	249.53	0.00	233.73	0.00	240.04	0.00

DISCUSSION OF RESULTS

## APPARATUS

Requirements. The magnitude of the quantity being measured must be considered when the success of this apparatus in dielectric dispersion measurements is contemplated. In the case of typical low molecular-weight substances, methyl and octyl alcohols, it has been reported that the dielectric constants change by factors of 15 and 2 respectively when the frequency is varied over a range of about 300-30 000 mc in the first case and 3-300 mc in the latter (14). This is a change in frequency by a factor of 100 in both cases. In contrast to this it has been found that in a 5% solution of ethyl cellulose the dielectric constant changes by a factor of 1.2 over a comparable range of frequencies. In dilute solutions of ethyl cellulose and 5% solutions of cellulose acetate this factor is less than 1.05 (71). In the dilute solutions of cellulose acetate studied in this investigation, a change of about 0.5 uuf in a total of about 240 uuf was found; this corresponds to a factor of about 1.002. When this is taken into consideration it becomes obvious that in order to determine a satisfactory dispersion curve for a dilute solution of cellulose acetate, much greater precision is required in the measuring apparatus than would be required to obtain similar information concerning low molecular-weight compounds.

Testing. The tests carried out indicated that the operation of the apparatus in its final state of development was satisfactory even when the stringent requirements indicated above were considered. When the results of the test runs are compared to those obtained

using solution against solvent, there appears to be little room for doubt that the effect noted should be attributed to the presence of the polymer molecules in the solvent. In fact, any other explanation of the observed phenomena would have to be regarded as very unlikely.

Advantages of Method. The use of two cells which were nearly identical electrically and mechanically was very advantageous, because the effect of such things as residual inductances, distributed capacitances and resistances of the leads and of the cells themselves tend to cancel. The effect of the finite dissipation factors of both solvent and solution also tend to cancel. The extent of the latter would obviously depend on the difference in the dissipation factors of the solvent and solution. Fortunately, in the system under consideration, this difference is negligibly small.

These desirable characteristics of the present method made possible a high degree of precision in the measurement of the total capacity of the cells and a high degree of accuracy in the measurement of the difference in capacitance between the two cells. No attempt was made to measure the total capacitance of either cell accurately, however, and no claim is made that such a measurement could be made with a high degree of accuracy. In any series of measurements, it is assumed that the total capacitance of the cell filled with solvent is accurately known even though it is not. It thus becomes an arbitrary standard and any inaccuracy in the determination of the absolute capacitance of the cell containing solvent (which must be done by an independent method) is passed on and appears as an inaccuracy in the total capacitance of

the cell containing solution. This is relatively unimportant, however, because the difference between the cells as a function of frequency is the important quantity, and the accuracy with which this difference can be determined is not sensitive to the absolute accuracy with which the total capacitance is determined.

Another similar consequence of this method is that the accuracy with which the difference between the two cells is determined is also much greater than the absolute accuracy of the calibration of the precision capacitor, if the range of values of  $C_{pII}$  is comparatively small, say 15 uuf.

It appears that the most important inherent advantage of the present method over other more common procedures is that frequency rather than voltage is the variable that goes through a "null", since frequency could be multiplied and counted with much greater accuracy and stability than the voltage out of a bridge can be amplified and detected by conventional means. The success of the present method should be attributed partly to the way in which the cells were switched in and out, and to the mechanical rigidity (and consequent electrical stability) which was finally attained. The importance of this has recently been emphasized (43).

Limitations of Method. One of the most serious limitations of this method is that it is not readily adaptable to the determination of the difference between the loss angles of the solvent and solution. The difference in signal voltages which results from exchanging the solution and solvent cells in the oscillator might be used as a measure of this

quantity, but the limiting device tends to offset this change and thus renders such a measurement quite insensitive. A very sensitive method would be required in order to obtain satisfactory results, because the change is such a small fraction of the total voltage.

Another limitation arises from the fact that the measurement would be adversely affected by an appreciable difference in the dissipation factors. This means that the use of high dielectric constant solvents would probably be difficult.

#### METHODS AND PROCEDURES

Fractionation. The fractionation was carried out by Levi in anticipation of a need for the molecular-weight distribution curve for the cellulose acetate sample which was used in this and several earlier investigations (53). The most important result, however, was that it provided a number of fractions, which were as sharp as can conveniently be obtained by fractional precipitation, and which cover a considerable range of molecular weights. They were of great value in the present investigation since they provided the material necessary for the establishment of the critical frequency-intrinsic viscosity relationship and represented an abundance of raw material for the preparation of the blends.

The results of the characterization of the fractions by means of the intrinsic viscosities can be considered as fairly accurate. Some difficulty arose from curvature in the  $\eta_{sp}/c$  vs  $c$  plots, but it was limited to comparatively few of the fractions having fairly high molecular weights. The cause of this is not known.



The precision achieved by the different operators was regarded as very satisfactory. Fractions having the same viscosities were combined for the purpose of calculating values of  $I_p$  for the distribution curve, but none of the fractions were physically combined. There was some inconvenience in handling such a large number of fractions, but fractions having as narrow a distribution as possible were desirable. It is conceivable that circumstances could exist where the distribution within fractions would not be increased by combining them, even though such circumstances are very improbable. The author cannot imagine circumstances, however, where combination of fractions would cause an over-all narrowing of the distributions of the fractions involved.

The results of the characterization of the fractions were not changed over to either molecular weights or degrees of polymerization, because the constants necessary to do this are not known with sufficient certainty to make such calculated quantities of any value greater than the intrinsic viscosities themselves.

Blends. The blends were prepared in order to supplement the information which could be obtained from dispersion measurements on the original material. This seemed particularly desirable after the rather irregular nature of the distribution of the original material became evident. In many respects, the preparation of artificial blends is advantageous. Blending of fractions is much simpler than fractionating blends from an experimental standpoint. It is also possible to prepare blends in which the molecular weight distribution is given by an equation which is more conducive to mathematical treatment than the

empirical equations which might be fitted to the naturally occurring distribution. Furthermore, there is the possibility of controlling the variables so that they can be studied separately, as was attempted in this investigation.

There is room for considerable question concerning the accuracy of the distribution curves of the blends. It is obvious that the accuracy is very limited, because it is tacitly assumed that the fractions have some sort of idealized distribution; and such an assumption cannot be justified. The author believes, however, that the distribution curves of the blends are known with as much accuracy as distribution curves of any material are known; because, in any case, the distribution curve is constructed mechanically from the information obtained from fractions which have unknown distributions.

#### EXPERIMENTAL RESULTS

Critical Frequency-Intrinsic Viscosity Relationship. A summary of the critical frequencies and the intrinsic viscosities determined for the fractions is given in Table 17. It was found that a log-log plot of the data exhibited some curvature, most of which could be removed by resorting to a plot of  $\log (fc+2)$  against  $\log ([\eta]+1)$ . This plot is given in Figure 9. The exact cause of the variation in the data is not known. Some of it can no doubt be attributed to error in the intrinsics while part of it may be due to inaccuracies in the determination of the critical frequencies. It should be noted, however, that the precision in determining the critical frequency did not indicate the presence of random inaccuracies of such a magnitude.

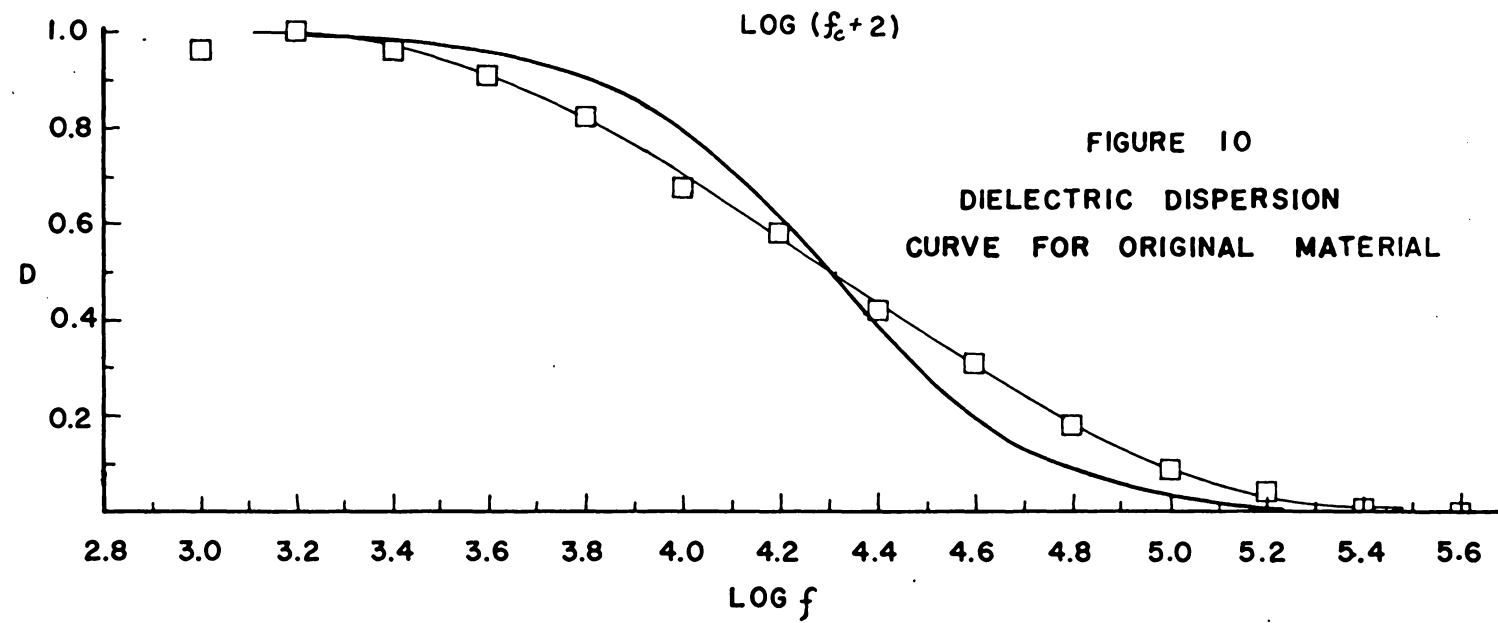
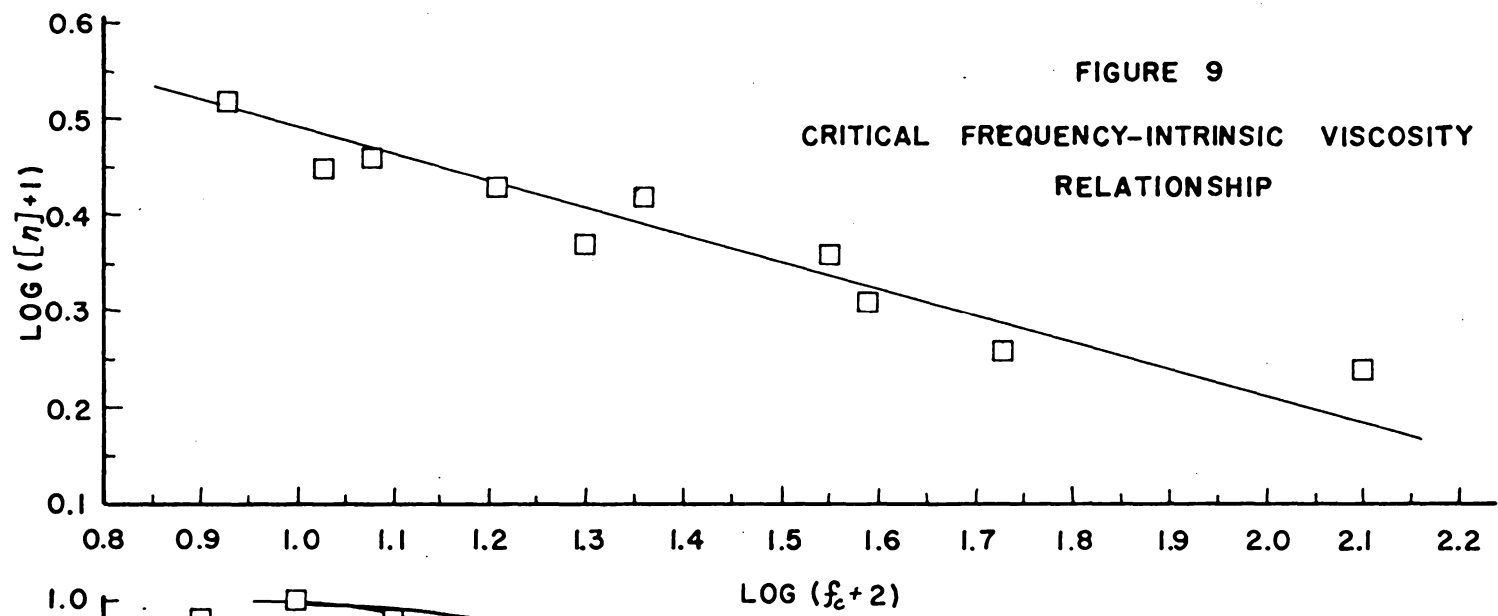


TABLE 17  
Intrinsic Viscosities and Critical Frequencies  
of Fractions

Fraction	$f_c(\text{kc})$	$\log(f_c + 2)$	$[\eta]$	$\log([\eta] + 1)$
21A	6.60	1.93	2.32	0.32
31B	8.72	2.03	1.84	0.45
12B	10.0	2.08	1.90	0.46
A	14.1	1.21	1.70	0.43
42C	17.8	1.30	1.37	0.37
12E	20.9	1.36	1.63	0.42
31C	33.1	1.55	1.30	0.36
41C	37.2	1.59	1.05	0.31
43B	51.3	1.73	0.82	0.26
22C	126.*	2.1	0.72	0.24

Fraction 22C was the only one for which the critical frequency could not be determined satisfactorily. The value given must be regarded as a rough estimate. It was disregarded in drawing the curve.

It can be seen from Figure 9 that the relation of critical frequency to intrinsic viscosity has the same form which had been found earlier for the relation between critical frequency and degree of polymerization (71). In fact, if the logarithms of the intrinsic viscosities obtained in the earlier work are plotted against the logarithms of the critical frequencies, the similarity of the two sets of data is striking. One difference, which becomes apparent when the data are compared, is that the reproducibility of critical frequencies was much greater in the present investigation but that the variations from one fraction to another is also much greater. Of more importance, however, is the fact that the critical frequencies in dilute solution were found to be about ten times as high as they were in the more concentrated solutions, for the same range of intrinsic viscosities. This is probably partly due to less entanglement of the chains and hence less restriction to rotation at the lower concentrations. It might also be partly attributed to the difference in solution viscosities at the two concentrations. The method used to determine  $C_0$  in the other investigation probably causes the critical frequencies to be lower than they should be also.

The equation relating the intrinsic viscosity and critical frequency which resulted from this investigation is:

$$\log([\eta] + 1) = 0.758 - 0.27 \log(f_c + 2). \quad (12)$$

Relation between Dispersion and Distribution Curves. The experimental results obtained on the blends are felt to be very satisfactory. Those for the original material are only slightly less satisfactory. It was run several times with results which are in good agreement among themselves, but the procedure was not as refined as it was when the blends were run. The utmost precautions were taken in running the blends and the agreement obtained between successive runs on the same blend was excellent in all cases. The results for the original material are plotted in Figure 10 and those for the blends in Figures 11, 12, and 13. The curves which are drawn in these figures are the theoretical Debye curves, and are included so that comparison between them and the experimental results is simplified. For the purpose of further comparison, the experimental results and theoretical Debye curve for fraction 41C are shown in Figure 14. This represents the closest agreement obtained between a dispersion curve for a fraction and the Debye curve.

All of the experimental evidence obtained thus far on cellulose acetate (71) and ethyl cellulose (69)(70)(72) indicates that the phenomenon is best described as Debye dispersion; that is, it occurs over a much wider range of frequencies than resonance dispersion which was indicated experimentally by the results of Scherer and Testerman on cellulose nitrate (73). In the case of Debye dispersion, the change in dielectric constant takes place over a relatively wide range of frequencies, even in the case of a single relaxation time. This can be attributed to decreasing polarization or orientation with increasing

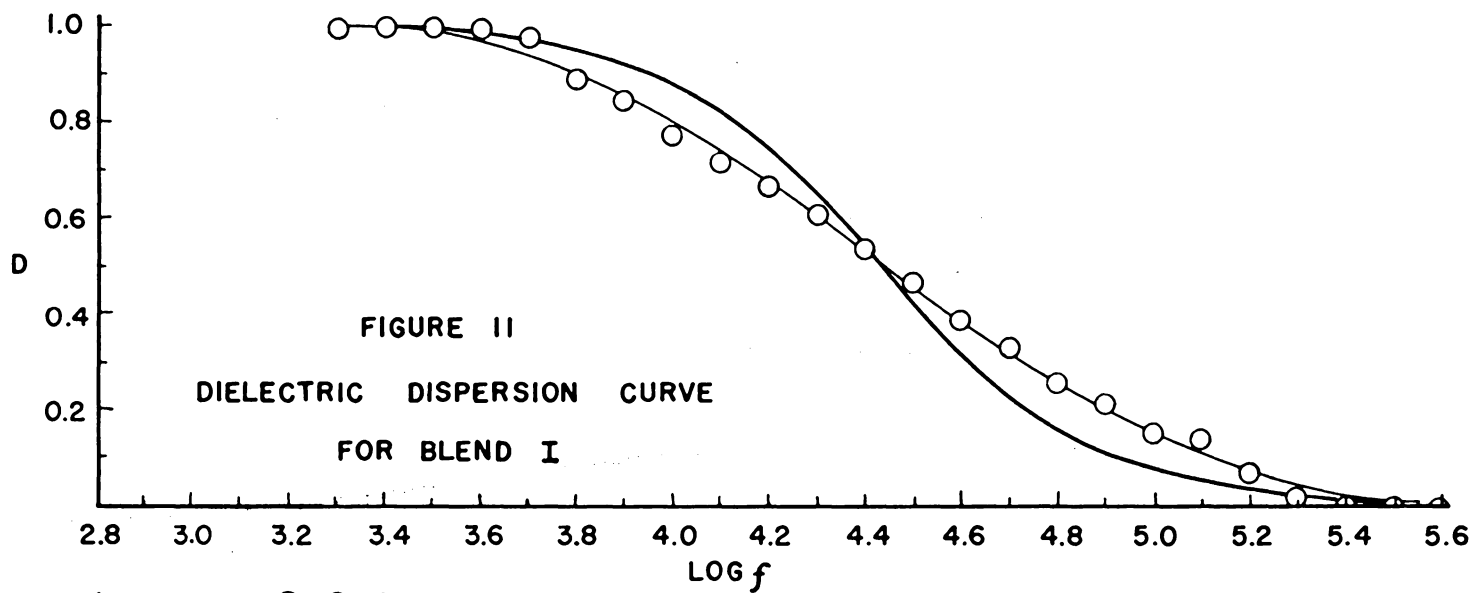


FIGURE 11  
DIELECTRIC DISPERSION CURVE  
FOR BLEND I

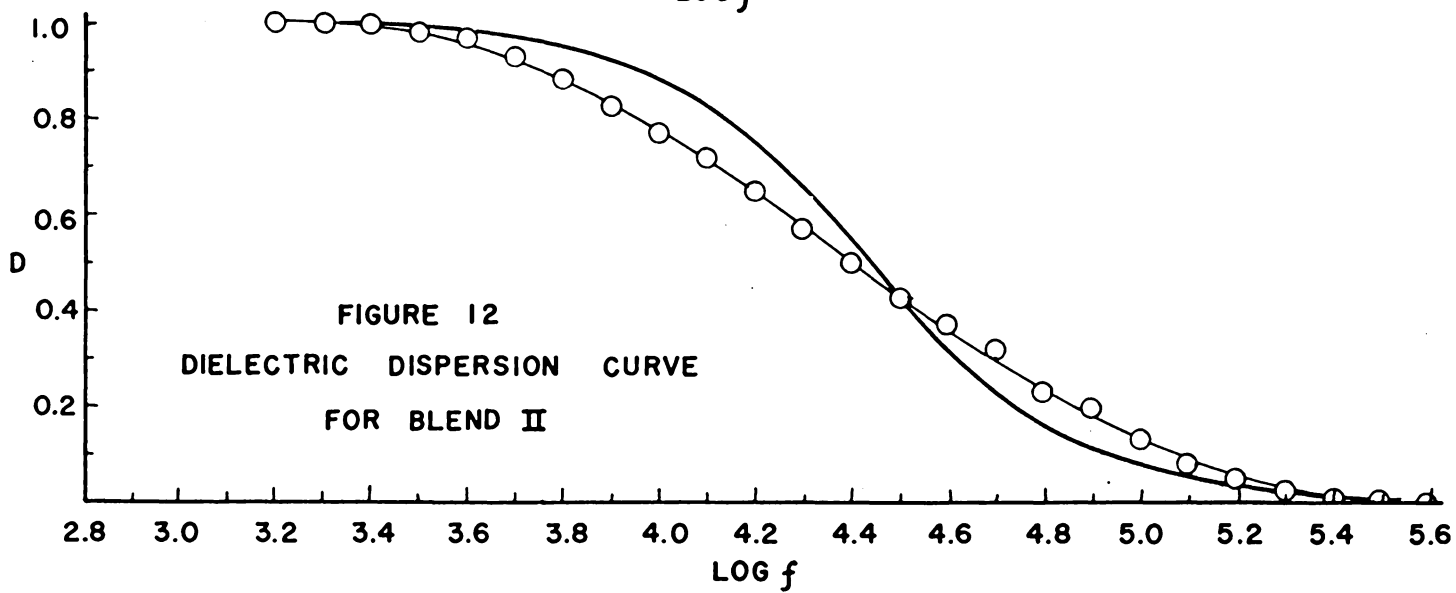
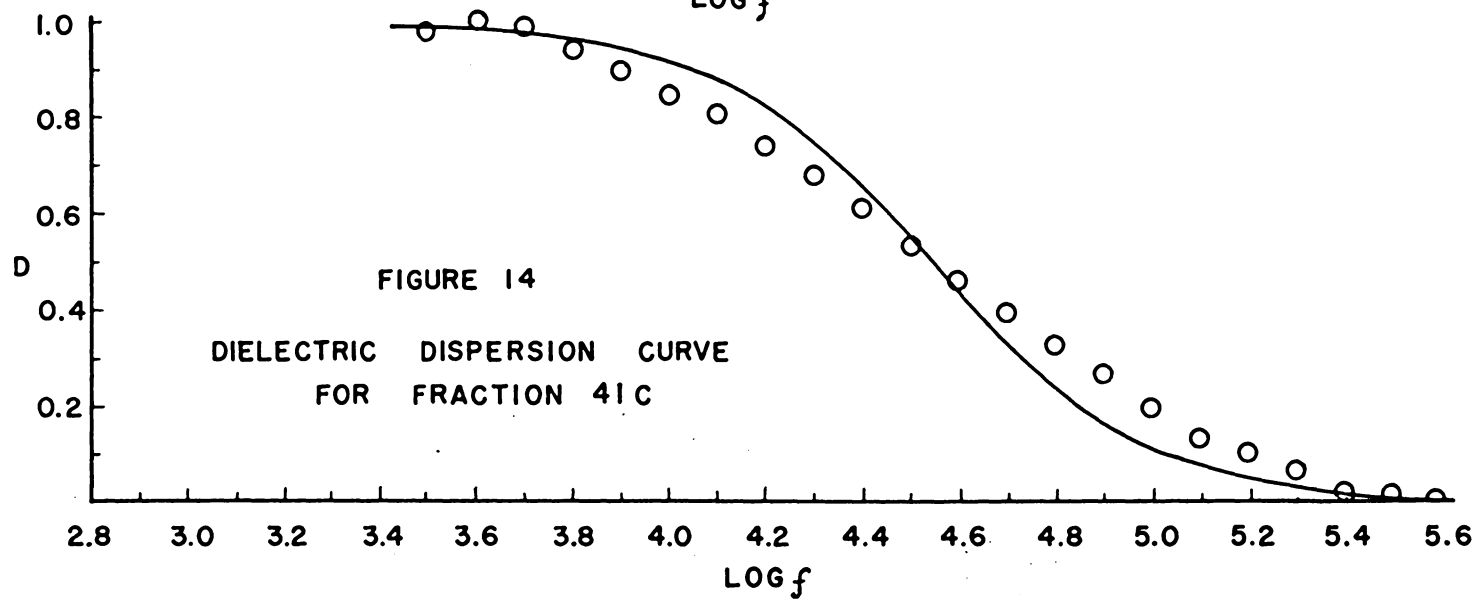
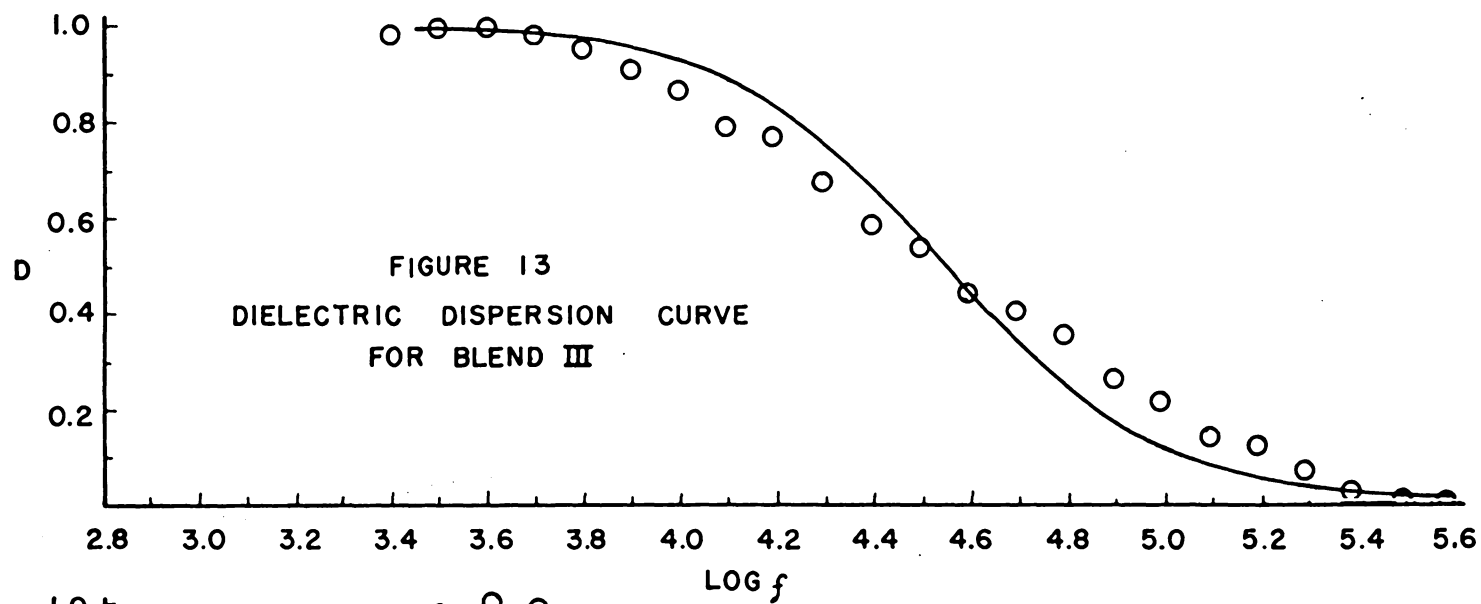


FIGURE 12  
DIELECTRIC DISPERSION CURVE  
FOR BLEND II





frequency, which results from the inability of the molecules to stay exactly in phase with an applied time varying field. At a given frequency, the phase difference depends on the resistance to rotation of the molecules which, in the case of solutions of rod-like cellulose derivatives, depends on the molecular size. Where there is a distribution of molecular sizes about some average value, there should also be a distribution of phase differences about some average value. This could be expected to show up as a broadening of the range of frequencies over which dispersion occurs.

It was hoped at the outset of this investigation that, if a dielectric dispersion curve of sufficient accuracy could be obtained, there might be indicated some relationship between the dispersion curve and the molecular weight distribution curve. Since the range of frequencies over which the dispersion takes place had been indicated experimentally to depend on the molecular size in the case of fractions, this expectation does not seem unreasonable, even though no relationship between the shapes of the curves has been found thus far. There is little doubt in the mind of the author that the shapes of these curves are related.

Examination of Figures 11, 12, 13, and 14, reveals that the expected results were not found. The results of the runs on the blends are more or less what was expected, but it was hoped that the dispersion curves for the fractions would follow the Debye curve rather closely. They do not. If the fractions had followed the Debye curve closely, it could have been concluded that the deviation from Debye dispersion

in the case of the original material and the blends was due solely to the effect of the greater molecular weight distribution in these samples. After this difficulty became apparent, fractions were deliberately selected in an attempt to get ones with small distributions, but the best results which could be obtained and reproduced are those in Figure 14.

In spite of all this, the effect of the width of the blends did show up in the experimental results. Examination of Figures 11, 12, and 13, indicates that the slope of the experimental dispersion curve at the critical frequency increases as the width of the molecular weight distribution decreases, that is, the slopes increase progressively for Blends I, II, and III. Consequently, the differences between the slope of the Debye curve and the experimental curves are in the same direction, the widths of the distributions having the ratio  $0.34 : 0.25 : 0.16$  while the difference in slopes are  $0.74 : 0.59 : 0.49$ . It must be noted again, however, that the dispersion curves obtained for the fractions in general do not confirm the conclusion that the differences between the experimental curves and the Debye curves are related to the widths of the distributions. In fact, the differences between the slopes were greater for several fractions than for Blend III, while that of Blend III was greater than would have been predicted from the results on Blends I and II.

The experimental results for the blends were also examined from some other points of view. It has been found that the empirical parameter,  $\alpha$ , introduced by Cole and Cole is a measure of the width of the distribution of relaxation times (12). Ordinarily  $\alpha$  is

determined from the plot of  $\epsilon'$  against  $\epsilon''$  as described in the "Literature Review" but it can be seen that it is also a function of the slope of the dispersion curve at the critical frequency. The frequency dependence of  $\epsilon'$  is given by:

$$\epsilon' = \epsilon_{\infty} + \frac{(\epsilon_0 - \epsilon_{\infty}) [1 + (f/f_c)^{1-\alpha} \sin(\frac{\alpha\pi}{2})]}{1 + 2(f/f_c)^{1-\alpha} \sin(\frac{\alpha\pi}{2}) + (f/f_c)^{2(1-\alpha)}} \quad (13)$$

It was thus possible to evaluate  $\alpha$  by solving for D and taking the derivative of the dispersion, D, with respect to  $\log f$  and plotting the result, for  $f$  equal to  $f_c$ , against  $\alpha$  by choosing arbitrary values of  $\alpha$ . The slope of the experimental curve at  $f_c$  could then be measured graphically and the corresponding value of  $\alpha$  determined from the plot of  $\alpha$  against the slope. After  $\alpha$  is determined, it is a relatively simple matter to calculate the dispersion curve predicted by equation (13).

The values of  $\alpha$  were determined by this method for all three blends. They are 0.25, 0.20, and 0.17, for Blends I, II, and III respectively. Using the value for Blend I, the dispersion curve was calculated and plotted, and it was found that equation (13) predicted dispersion over a very much wider band of frequencies that had been found experimentally. It must be concluded from this that the distribution of relaxation times in this case is not fully described by (13). On the other hand, it seems safe to conclude that the trend in the values of  $\alpha$  for the three blends does follow that of the widths of the molecular weight distributions.

It appeared that the dispersion data for the fractions might be explained by assuming that the apparent distribution of relaxation times was due to flexibility of the chains. Such an assumption is not completely unreasonable. The stiffness of the chains of the cellulose derivatives was discussed in the "Literature Review" where it was pointed out that for values of DP less than 100, the chain was relatively stiff; whereas, chains having DP's greater than 500 could be considered as random coils. The DP of this material is not known with certainty.

On the basis of viscosity measurements by Awni (2) and Hawkins (39), however, it seems that the fractions used in this investigation cover a range of DP from about 70 to about 250. It is thus possible that some of these fractions could be in a DP range where they would show some flexibility.

As was also pointed out in the "Literature Review", the case of completely flexible chains was treated by Kirkwood and Fuoss (50) and an equation derived which described the behavior of poly-(vinyl acetate) more or less quantitatively. The expression obtained by these authors is:

$$J(x) = \frac{1}{(1+x^2)^2} \left\{ 1 + x^2 + \frac{\pi x}{2} (x-1)^2 - 2x^2 \ln x \right\} \quad (14)$$

where

$$x = \frac{f}{f_c} \quad (15)$$

and  $J(x)$  is the same as the dispersion,  $D$ .

The curve corresponding to this equation was calculated for fraction 41C which had a critical frequency of 42.7 kc, and it was found that the dispersion region corresponding to this equation was much wider than that indicated by experiment. It was wider even than the one corresponding to equation (13). This result indicates that, even in the case of the highest DP fraction investigated, the behavior is quite different from that predicted for a random coil.

During the course of the investigation of fractions, it was noticed that the magnitude of the change in dielectric constant of the solutions seemed to depend on the concentration and to be essentially independent of the DP. This is shown in Table 18 where the ratio of  $\Delta C$ , the total change in capacitance of the cell, to  $c$ , the solution concentration, can be seen to vary about an average value of 0.62 in a manner which does not seem to indicate much effect of the DP. This behavior has been found in other cases, also. It thus appears that the dispersion due to any particular molecular species depends only on the weight of that species present, at least to a fair approximation.

If it is assumed that this is actually true, it is possible to construct a curve from a known molecular weight distribution curve, if it is further assumed that pure Debye dispersion would be obtained in the case of a single molecular species. This can be done by starting with the theoretical distribution for one of the blends and arbitrarily selecting several viscosities symmetrically located with respect to the average value. The theoretical weight of each of the selected species

TABLE 18

Solution Concentrations and Capacitance

Changes for Fractions

Fraction	Concentration gm./100ml.	c uuf	$\frac{\Delta c}{\text{conc}}$
21A	0.46	0.34	0.74
31B	0.50	0.32	0.64
12B	0.76	0.51	0.67
	0.38	0.25	0.66
A	0.59	0.66	1.1
42C	0.59	0.52	0.88
12E	0.63	0.31	0.49
	0.54	0.47	0.87
31C	0.51	0.29	0.57
41C	0.61	0.35	0.57
43B	0.61	0.37	0.61

present in the blend can then be calculated. The critical frequency of each species selected can be determined from the experimentally determined relationship between intrinsic viscosity and critical frequency, and these critical frequencies can be used to calculate the theoretical Debye curves of each species. Knowing the dispersion curve of a particular species, the concentration of the species, and the ratio of  $\Delta C$  to  $c$ , it is then possible to calculate the change in total capacitance due to each of the species selected, as a function of frequency. Having this information it is then possible to sum the contributions due to each of the species at a number of frequencies and thus to determine a theoretical dielectric dispersion curve.

These calculations were carried out on Blend I and it was found that the deviation from the Debye curve should be much less than was indicated experimentally. In fact, the deviation indicated on the basis of these calculations was less than that observed experimentally for fractions. If this represents the total effect of the distribution of molecular weights, the construction of the molecular weight distribution curve from the dielectric dispersion curve would necessitate determination of the dispersion curve with even more precision than was attained in this investigation.

These results can be explained in two ways. It is entirely possible that, even though the flexibility of the chains is not great enough to give agreement with an equation developed on the basis of random coils, the deviation from the Debye curve is due to a slight flexibility of the polymer chains. Since very high DP cellulose acetate

behaves like a random coil and very low DP cellulose acetate behaves like a rigid rod, intermediate values of DP would have to be expected to exhibit some sort of intermediate behavior which would be neither that expected of random coils nor that expected of rigid rods. Whether or not this is actually the case, might be determined experimentally by investigating fractions covering a very wide range of DP. It would be expected that very high DP fractions would give dispersion curves of the type found in this investigation while very low DP fractions should give curves which might follow the theoretical Debye curve more closely. This did not show up in the range of DP covered in this investigation, but the range that could be covered was a rather narrow one.

A second explanation of these results comes from consideration of the quality of the fractions used. The author feels that the fractions obtained by Levi are as sharp as can be expected from fractional precipitation techniques, but apparently there is room for question as to how good a technique fractional precipitation is. It has been tacitly assumed in most of the foregoing discussion that the fractions represented single molecular species. Such an assumption is justified by neither experiment nor theory, but it is usually regarded as a fair approximation. It is thus possible that the fractions and blends both represent very much wider distributions than those upon which the above discussion and calculations are based, and this could account for the behavior of the fractions.



A combination of these two effects is possible, of course, and it seems quite likely that they both are operative to some extent.

CONCLUSIONS

It is possible to draw three definite conclusions from this investigation. One is that the method of measurement developed here is capable of satisfactory results. The second is that the critical frequencies determined for dilute solutions of cellulose acetate fractions in dioxane are related to the intrinsic viscosities of the fractions. The third conclusion is that the slope of the dielectric dispersion curve is related to the width of the molecular weight distribution in some way. Based on the latter two conclusions, it can be further concluded that it is very probable that the over-all shape of the dielectric dispersion curve has some relationship to the shape of the molecular weight distribution.

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation of the encouragement, assistance, and guidance given by Dr. P. C. Scherer and Dr. D. W. Levi during the course of this investigation. The time spent by Dr. C. A. Holt of the Department of Electrical Engineering in consultation with the author is also gratefully acknowledged.

This investigation was sponsored by the Office of Ordnance Research, U. S. Army.

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## ABSTRACT

Previous investigations have revealed that some polymer solutions exhibit dielectric dispersion (variation of the dielectric constant with frequency) which is apparently related in some way to the molecular weight of the polymer (1) (2) (3). One of these investigations (1) was carried out on solutions of cellulose acetate in dioxane. It was found that the change in dielectric constant was so small that rather concentrated solutions had to be used in order to obtain reproducible results. The possibility of intermolecular interactions in concentrated solutions made dilute solution measurements desirable. Consequently, the object of the present investigation was to carry out such measurements with sufficient precision to define the shape of the dielectric dispersion curve over the necessary frequency range.

The fundamental difficulty was that the change in dielectric constant of a solution containing less than 1% cellulose acetate was only about one part in five hundred or less in a frequency range of about three decades. The course of such a small change is difficult to detect over such a wide band of frequencies. Capacitance bridges, which are very good for making measurements at a single frequency, particularly in the range of frequencies under investigation; were commercially available. However, bridges have certain inherent disadvantages which make difficult the coverage of such a wide band of frequencies with the necessary precision. The use of ordinary resonance methods was desirable, but they are limited by the practical sizes of the components to frequencies well above the lowest frequencies which

were expected to be encountered. As a result of these limitations, a modified resonance procedure was adopted. A resistance-capacitance oscillator was substituted for the more conventional inductance-capacitance circuits. Null indications were obtained by substituting a frequency counting system of great precision for the "zero beat" method.

It had been found earlier that the critical frequency was related to the weight average molecular weight of the polymer sample, the critical frequency being defined as the frequency at which the dispersion was 0.5. Based on this it seemed reasonable to assume that the dielectric dispersion curve might be related in some way to the molecular weight distribution curve in the case of a polydisperse sample. An attempt was thus made to obtain the dielectric dispersion curve in as much detail as possible, since this served the two-fold purpose of permitting conclusions to be drawn concerning the validity of the molecular weight relationship in dilute solutions and giving an indication of any influence of the molecular weight distribution on the dielectric dispersion.

Apparatus was developed which gave a precision of 0.01 uuf in a total of about 250 uuf. This provided the means of measurement. Measurements were made on several fractions and three artificial blends.

The results of measurements on fractions indicated that the form of the critical frequency-molecular weight relationship determined earlier (1) was correct. The dispersion curves obtained for the three blends of varying width indicated that the slope of the dispersion curve at the critical frequency decreased as the width of the

blend was increased. This was the only indication of an influence of the width of the distribution on the dispersion curve. It was noted, however, that the slopes of the dispersion curves for the fractions were less than those for the narrowest blend in several cases. The most reasonable explanation of this observation seems to be that the fractions and blends have much wider distributions than was believed. It is also possible that chain flexibility might be a complicating factor.

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