DIELECTRIC DISPERSION OF ETHYL CELLULOSE SOLUTIONS

by

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Dedicated to my wife, Dot,
without whose help
this work would not
have been possible.

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INTRODUCTION

INTRODUCTION

An insight into the behavior of high polymers in solution is constantly being sought. To explain and predict the behavior of plastic products we must know the shape and size of the chains that make up our plastic. Possibly the most important of the two above-mentioned properties is the size. The molecular weight is a measure of the size.

Methods that can be used to measure the molecular weight should be extremely important and valuable tools in the polymer field. There are many known methods of molecular weight determination but only a small number of these are applicable to high polymeric materials due to the enormous size of polymer molecules which ranges anywhere from 1,000 to 12 million in molecular weight.

For this reason this investigation was carried out. Any new method would be a giant stride in the technology of today. Even more remarkable and valuable would be a method that can be used to obtain the molecular weight rapidly as well as accurately.

An indication that this method would be applicable to high polymers was developed in the author's Master of Science thesis (46). The purpose of the present research was to determine:

(1) The application of the method to other cellulosics as well as the investigation of the effect of various solvents.

(2) To study the effect of different solvents on the configuration and dispersion of the high polymer in solutions.

This work, due to time requirements, must be confined to ethyl cellulose systems, but work is under way by various investigators at the present time on other systems (48).

Investigations concerning the solvent seem a very important phase of this work since, from a theoretical point of view, the configuration of polymer molecules in solution is quite revealing as to polymer behavior.

In this investigation relatively dilute solutions were used because it was thought that in such dilute solutions the chains are able to act independently of one another.

No satisfactory constants are available in the literature for the conversion of the intrinsic viscosity of ethyl cellulose to the molecular weight. For this reason dielectric dispersion measurements were compared with the experimental intrinsic viscosity. It will be shown in a later section that the molecular weight obtained by the dispersion method is apparently similar to a viscosity average molecular weight.

Results up to the present time lead one to believe that this method shows great promise in the field of molecular weight determination. Possibly it will also give a quick and very accurate determination of molecular weight distribution curves of either homogeneous or heterogeneous polymer samples. Even at this early stage a narrow or broad distribution can be differentiated with little difficulty. It is being considered at the present time for use in controlling polymerization processes (12).

A great deal of work must yet be done but great promise is shown to date. Very interesting and informative results will certainly be derived from determinations that should help one to better understand the materials that are called our plastic products. Information of this nature should broaden the use of these products through knowledge of the possible size and chain configuration.

As was mentioned earlier, the time required for measurement should be the feature that makes the dielectric dispersion method very useful and acceptable.

LITERATURE REVIEW

CELLULOSE

Cellulose is commonly referred to as a natural high polymer that is a mixture of homologous polymeric materials (81). Cellulose is a compound that is produced by plants by such a process that chemists are unable to reproduce it.

Today without many exceptions people recognize and accept the Haworth structure as being the correct interpretation (Figure 1). Evidence for and against such a structure can be found in any text of cellulose chemistry and for that reason will not be discussed here (53).

Through a degradation process it was found that cellulose was composed of β anhydroglucose units and that the alternate glucose units were inverted. They were joined through oxygen bridges at the number one carbon of one ring to the number four carbon of the next ring (53)(83)(61). This inversion of glucose units was necessary for the units to lie in the same plane.

The individual cellulose chains are held together by forces. These forces might be either Van der Waals forces, resonance bonding, or hydrogen bonding. It is known that all of the chains are not perfectly aligned since crystalline and amorphous regions occur in x-ray diagrams (75)(77)(53).

It has been established that the groups on the end of the cellulose chain are different from the inner groups in

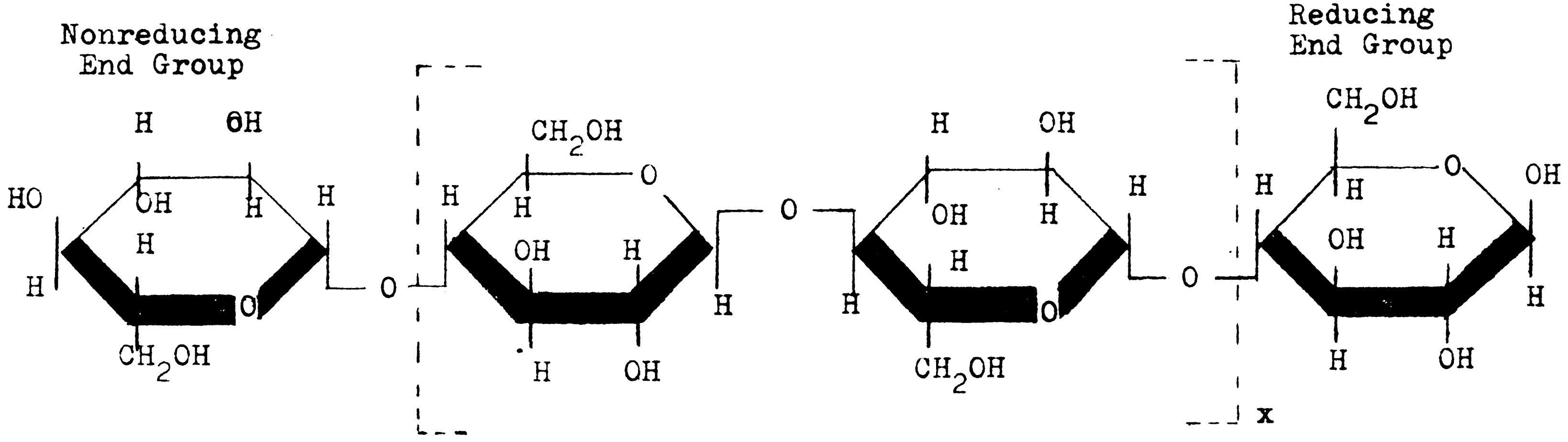


FIGURE 1. THEORETICAL CONFIGURATION OF THE CELLULOSE MOLECULE

D. P. = 2x + 2

that one of the end groups is a reducing group (10)(47). The other end glucose ring contains four hydroxyl groups.

Cellulose is a polymer that is used in the preparation of many derivatives since it will undergo most reactions that an organic alcohol will undergo and the 2, 3 and 6 positions are substituted during esterification, or etherification (51).

ETHYL CELLULOSE

One of the most important products obtained from the etherification of cellulose is the ethyl ether, or what may be referred to as ethyl cellulose. This product is used in large amounts in industry for fibers, molded articles, coatings, lacquers, and varnishes. These many uses demand that the polymer be tough and have a high strength and stability. It can be extruded, injection molded, compression molded and cast.

Ethyl cellulose may be prepared by first treating the native cellulose with an 18% NaOH solution. Soda cellulose is formed (52)(74) and treated with ethyl chloride (57). The principal reactions may be expressed as:

$$\mathrm{Cell(OH) + NaOH = Cell\ (ONa) + H_2O}$$

$$\mathrm{Cell(ONa) + ClC_2H_5 = Cell(OC_2H_5) + NaCl}$$

Side reactions also occur depending on the ratio of the cellulose and water. The greater the ratio the greater the side reactions.

Also the ratio of NaOH to H_2O is important in that it influences the degree of substitution.

Diethyl sulfate is used on a small scale for the preparation of ethyl cellulose (56). The possible reaction may be shown in the following manner:

$$\mathrm{Cell(ONa)} + (C_2H_5)_2SO_4 = \mathrm{Cell}(OC_2H_5) + \begin{matrix} NaO \\ C_2H_5O \end{matrix}\!\!> SO_2$$

Substitution does not occur in a uniform manner but in a completely random one. This may be attributed to the fact that all of the hydroxyl groups have equal probability of reacting. According to Spurlin (105):

> "the substituents in the cellulose derivative are distributed among the hydroxyls according to the laws of chance, and the three sorts of hydroxyls are substituted to an extent relative to one another that is (determined by the relative reactivities of the hydroxyls determined by their inherent properties as well as by the reaction medium) and the nature of the reaction (proceeding to an equilibrium at a partially substituted state, or with a tendency to proceed to complete substitution, but stop at a partial substituted state)."

The number of unreacted hydroxyl groups may be determined by tosylation-iodination and the degree of substitution thus determined. Ethyl cellulose may be obtained in many different degrees of substitution. The common commercial product has a D.S. of 2.20 - 2.58 which corresponds to 44.0 - 49.5% reaction. High degrees of substitution yield a D.S. of 2.60 - 2.80 which is 50.0 - 52.5%. Low conversion can be expressed as 0.8 - 1.7 or 19.0 - 35.0% (91).

Ethyl cellulosics of higher degrees of substitution are uniform in the distribution of the alkyl group. This was proven by Okamura (85) and McNeer (79) by a fractionation procedure. Both obtained fractions that varied only slightly in degree of substitution with different molecular weights.

Ethyl cellulose, as is true with other polymers, natural and synthetic, should be fractionated to be theoretically studied. For this reason the theories of fractionation should be mentioned later.

CONFIGURATION OF CELLULOSE AND ITS DERIVATIVES IN DILUTE SOLUTION

The accepted picture of high polymers in solution, whether cellulosic or otherwise, is that the individual chains or molecules are completely dispersed. This means that solvent has entered between each chain and broken whatever bonds that existed. If there is any occasional association, the bond is broken by forces existing in solution (107).

In the establishment of a picture pertaining to cellulose and its derivatives it is necessary to consider the work done on this subject and the conclusions reached by each investigator as a result of his work. Any work considered can be applied to either cellulose or its derivatives since the difference lies only in the fact that hydroxyl groups have been substituted. The existence of rotation around the ether bond in the chain is possible in either structure.

Investigation by W. & H. Kuhn (66) showed that cellulose molecules in solution did not have a high degree of coiling but were more rigid in nature.

Work by Pelson (93) showed that the dissymmetry factor was larger than that expected for a random coil polymer.

Kuhn (67)(68) treated the subject statistically. He showed that, in the case of molecules adhering to the rigid rod configuration, the molecular weight should be directly proportional to the length. Bridgeman (9) by investigation was able to substantiate this theoretical work by consideration of the relaxation times. From his work he proved that the dispersion region for the cellulosics must lie in the region in which Kuhn predicted them. Cellulose fell into this predicted region and thus was considered to be somewhat rigid in nature.

Light scattering has proven very enlightening as far as solution configuration is concerned. Blaker and Badger (4) determined with fractionated cellulose nitrate that if the D.P. exceeded 100, the cellulose molecule approached a random coil configuration. If 100 or less, the chain behaved as a rigid rod and could be so treated in the calculation of molecular weight by light scattering.

Stein and Doty (111) determined that cellulose acetate existed in the rigid rod configuration up to a molecular weight of 80,000. If the molecular weight by light scattering exceeded this, the chain doubled back on itself and thus assumed a random coil configuration.

Viscosity is considered a reliable tool in determining configuration since in the modified Staudinger equation

$$[\eta] = KM^a$$

if the "a" is 1.0, or closely approaches such a unity value, the polymer molecule is considered a rigid rod in solution. For random coils the value is 0.5 and approaches unity as the chain becomes a stiffer rod.

Solvent determines the configuration in many instances as well as the effective length of the chain. As the solvent becomes increasingly better, the chain should be more fully extended due to the fact that the interaction of the polymer and solvent is greater than either the polymer or solvent for itself.

It would thus appear that the polymer chain length, as well as solvent, play equally important roles in configuration. If the polymer does not have a molecular weight over 70,000 - 80,000 and the solvent is good, it is then quite possible to assume a rigid rod configuration.

METHODS OF FRACTIONATION

Bearing in mind that polymers are a heterogeneous mixture of chain lengths, one turns to fractionation. This is an attempt to separate the heterogeneous polymer into groups which are homogeneous with respect to chain lengths. This is not wholly possible but can be approached within limits of ±10% from the true mean (91).

Upon completion of a fractionation procedure an integral distribution curve may be obtained. An integral distribution curve is obtained by plotting molecular weight versus the value of Ip. Ip is found by adding to one-half of the weight percentage of each fraction the sum of the weight percentages of all preceding fractions starting with the lowest D.P. Differentiating an integral distribution curve yields a differential distribution curve. This represents the probability of finding a chain of given length in a heterogeneous polymer.

There are a number of methods that are used in fractionation. The fractional precipitation method is widely used today. The heterogeneous polymer is dissolved in a suitable solvent and then partially precipitated by means of the addition of a non solvent and often a lowering of the temperature. Proper adjustments of the amounts of non solvent and solvent give a two-phase system, the supernatant and precipitated phase. The success of the fractional precipitation procedure is the ability to choose the correct solvent - non solvent system. It is possible to choose the correct system by means of titrating the non solvent into a solution of the polymer until a slight turbidity is noticed (2)(34).

The fractional solution method depends on the solubility of polymer molecules (53). The polymer is placed into contact with a solvent and non solvent mixture until equilibrium is reached (30)(31)(98).

The molecular distillation method is useful primarily as a purification technique but can be employed in fractionation (18).

The ultracentrifuge is an excellent method, and its only drawback can be described as its failure to handle large enough samples. It is, therefore, more of an analytical technique but can be used very accurately for establishing molecular weight distribution curves (118).

Diffusion methods are based on the fact that lighter molecules will diffuse through a solvent layer before the heavier chains (18)(50).

Considerable work has been done in regard to ethyl cellulose. Several systems could be noted which gave favorable results. Most of the successful work was accomplished with a fractional precipitation procedure.

Okamura dissolved ethyl cellulose in acetic acid and then precipitated it by adding certain amounts of the non solvent water (85). Staudinger and Reinecke used dioxane - water systems (110); Scherer and McNeer (99) used a mixture of ethyl acetate and acetone as a solvent and water as non solvent; Scherer and Iacoviello (96) used different solvent - non solvent systems depending upon the degree of substitution.

METHODS OF MOLECULAR WEIGHT DETERMINATION

One of the most important aspects of polymer chemistry is the determination of molecular weight. As has been mentioned, many of the properties and uses of a plastic depend on the size of the molecules.

The purpose of the following research was to develop a method of molecular weight determination. For this reason a review of the existing methods of molecular weight determination should be briefly considered.

The fact must be borne in mind that polymers are heterogeneous mixtures of chain lengths and for this reason the molecular weight determination can only be an average. The existing methods can only give a molecular weight that is accurate to ±5.0% at best. Another difficulty which exists is that different molecular weight methods do not agree in many cases for the same polymer sample.

Bearing these short-comings in mind, there exist three different kinds of molecular weight averages. Number average molecular weights include such methods as osmotic pressure and end group determinations. Ultracentrifuge and light scattering are weight average methods. The viscosity method gives what is referred to as a vicosity or possibly "C" average. A doubt exists as to the exact category of the dielectric dispersion method.

As a basis of definition the number average depends on counting the number of particles that are present. The number average molecular weight in equation form is:

$$\bar{M}_n = \frac{\Sigma n_i m_i}{\Sigma n_i}$$

where n_i is the number and m_i is the molecular weight of the ith species

On the other hand, the weight average molecular weight is dependent upon the actual weight of the particle. The equation for the above may be expressed as:

$$\bar{M}_w = \frac{\sum n_i m_i^2}{\sum n_i m_i}$$

where the symbols used are the same as above.

The number and weight average molecular weights may be the same or one hundred percent different depending on the homogeneity of the sample.

The most reliable method for determining the number average molecular weight is the osmotic pressure method. It is one of the oldest used today and has proven itself to be accurate within the limits of error. This method, however, is often carried out in conjunction with other methods.

At infinite dilution the osmotic pressure is proportional to the number of particles present, and the molecular weight is inversely proportional to the osmotic pressure as given by Van't Hoff's law.

$$\pi/c = RT/M$$

where π = osmotic pressure

C = concentration

M = molecular weight of the solute

R = gas constant

T = absolute temperature

The molecular weight may simply be determined by plotting π/c versus C and extrapolating to infinite dilution. At this point the reciprocal is taken and the molecular weight is obtained.

This method is especially applicable to lower molecular weight high polymers. As the molecular weight increases the choice of a membrane for use in the osmometer becomes exceedingly difficult (6)(35)(81)(91)(103).

The chemical end group method is another applicable number average molecular weight method. This is one of the earlier methods but has been surpassed in accuracy and reliability by other methods. If a certain group is known to exist on the end of a chain and it may be detected through its chemical properties, the molecular weight can be determined. In the case of the cellulosics the molecular weight is measured by determination of a copper or iodine number. This enables one to actually count the number of end groups present and thus the number of chains (6)(58).

The weight average molecular weight is preferred by many investigators. For this reason light scattering measurements are very important and frequently appear in the chemical literature of today. Light scattering not only is a satisfactory method for molecular weight determination but also gives much valuable information regarding the shape of the molecule in solution.

The method is based simply on the scattering of light by particles. The larger the particle, the greater the amount of light it scatters. From the scattered light, τ , the turbidity is measured. By making a plot of Hc/τ versus concentration the molecular weight is the reciprocal of the

Hc/τ at infinite dilution. The equation for molecular weight involving turbidity concentration and the constant H is (8):

$$Hc/\tau = 1/M + 2BC$$

where B = second virial coefficient

$H = 32\pi^3 n_0^2 (n - n_0)^2 / c^2 / 3\lambda^4 N$

where C = solution concentration in grams/ml.

n = refractive index of solution

n_0 = refractive index of solvent

λ = wavelength of the incident light in cm.

N = 6.023×10^{23}

Many times a polymer solution presents difficulties that arise from too high a dissymmetry or a combination of other problems. In this connection Zimm plots are advised. These lead to great accuracy as an extrapolation to zero angle is made. An equivalent term to Hc/τ, Kc/R_θ is plotted versus $\sin^2\theta/2 + kc$. The molecular weight is the reciprocal of the extrapolated value. The result of such a plot is a grid-like graph. The accuracy in this determination stems from two factors. First, measurements are made at more angles (from 30° to 145°) and second, a double extrapolation is necessary. Number average as well as weight average may be obtained in certain cases (106).

The ultracentrifuge or sedimentation method makes use of a high speed centrifuge which measures the rate of sedimentation of the colloidal particles. The objection to this method is the great cost of the instrument and difficult technique. Even though the measurement gives weight average molecular weight, it will also lead to an accurate concept of the homogeneity of the sample (65). Particle shape, solvation and impurities can be evaluated.

By an observation of the change in concentration with time along a column the diffusion constant can be determined. Evaluating the velocity of sedimentation, the molecular weight then follows from: (6)(35)(53)(81)(91)

$$M = \frac{RTS}{D(1-Ve)}$$

where D = diffusion rate

S = sedimentation constant

V = partial specific volume of solute

e = density of solution

M = molecular weight

Perhaps the most widely used method of molecular weight determination is the viscosity method since it is the simplest, yet very reliable. Viscosity is a measurement of the resistance of motion of one layer of liquid as it passes over another which increases as the molecular weight increases due to the resistance to flow offered by the solute molecules. In dilute solution the molecular weight can be determined (6) (53). This method was developed by H. Staudinger (6)(53)(91) (108)(109) who stated that at low concentrations if a polymer is rod shaped, the weight average molecular weight is proportional to the specific viscosity:

$$\eta_{sp}/c = KM + K'P$$

or

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_{rel} - 1$$

where η_{sp} = specific viscosity

η = viscosity of polymer solution

η_0 = viscosity of pure solvent

η_{rel} = relative viscosity

K & K' = constants

M = molecular weight

P = degree of polymerization

C = concentration in grams per 100 ml.

This equation of Staudinger's is based on assumptions the validity of which is doubted over the whole range. 1. Cellulose and its derivatives must be dispersed in the form of a single molecule. 2. Viscosity measurements are independent of the nature of the solvent. 3. The expression η_{sp}/c is independent of C (3)(5)(7).

Kraemer (116) realized that all results did not agree and introduced the term intrinsic viscosity $[\eta]$ which is the limiting value or extrapolation of η_{sp}/c to infinite dilution.

$$[\eta] = \lim_{c \to 0} \eta_{sp}/c = \lim_{c \to 0} \frac{\eta_{rel} - 1}{c}$$

The Staudinger equation then becomes:

$$[\eta] = KM^a$$

where $[\eta]$ = the intrinsic viscosity

K & a = constants

M = molecular weight

It has been shown that "a" should be 0.5 for random coil molecules and approach 1.0 as the molecules become more rod like in nature (102). Light scattering and ultracentrifuge studies may be used to determine the constants "K" and "a".

The most recent method for calculation of molecular weight is the method of dielectric dispersion. As has been shown in the author's Master of Science thesis (46), this method is applicable to cellulose acetate. It will be shown later that it is likewise applicable in the case of ethyl cellulose. The method is based on the fact that chains follow an alternating current field until a point is reached where they are unable to do so. This causes a decrease in capacity which can be measured and related to the frequency. The empirical equation that is used can be shown to be:

$$\log M.W. = A + B (\log \nu_c + 1)$$

where A and B = constants

M.W. = molecular weight

ν_c = critical frequency

The critical frequency is the point at which the dispersion is fifty percent completed.

In discussion of results it will be shown why the molecular weight obtained is similar to a viscosity or "C" average.

DIELECTRIC DISPERSION AND LOSS

Static Dielectric Constant

The presently accepted interpretation of dielectric behavior owes a great deal to the theory of Debye (24) and subsequent refinements of his work.

In considering dielectric phenomena the static dielectric constant should be briefly considered since many equations were derived from it. From the dielectric constant the dielectric dispersion can be obtained and better understood.

The dielectric constant may be expressed as the force between the two point charges e and e' separated by distance "r" in a homogeneous unbounded dielectric. The dielectric constant is measurable by obtaining the ratio of the capacitance of a condenser filled with an unknown to the value filled with air.

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

Debye by a development of the Clausius-Mosotti equation developed an equation for the molar polarization by considering one possible situation of a molecule in a field (104). This was that of a cavity field. The cavity considered was a cylindrical cavity between two plates very near to each other. From the equation below the dielectric constant can be obtained as will be shown later.

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

where P = molar polarization

d = density

M = molecular weight

N = number of molecules per mole

α = distortion polarization

α_0 = polarizability

μ = dipole moment

ϵ = dielectric constant

By substituting $\epsilon = n^2$, where n is the refractive index, the Lorentz-Lorenz expression is obtained for the molar polarization.

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

There are, however, certain limitations or objections (13) to the equation in the present form.

According to the Debye equation there should be a linear dependence of the polarization upon the reciprocal of the absolute temperature. This is shown by gases, some polar liquids, and solids, where a certain degree of molecular freedom exists. If there is any degree of hindered rotation, the Debye equation is not accurate for known measurable values. For instance, the Debye equation can be shown to predict ferroelectric behavior of water throughout the entire liquid range. The Debye equation holds when $\epsilon = \epsilon_\infty$. In gases $\epsilon_\infty = 1$ as well as $\epsilon = 1$.

Debye's equation takes into account only a single relaxation time rather than a distribution of such which is known to be present in many substances. Also, in the Debye equation, the shape of molecules is not taken into account nor is the existence of a macroscopic viscosity. Many attempts have been made to modify the Debye equation and in doing so to obviate some of the difficulties.

Van Arkel and Snoek (119) developed a semi-empirical equation which introduced into the denominator the dipole-dipole interaction energy of molecules and apparently eliminated ferroelectric behavior.

$$(3)\quad \frac{\epsilon-1}{\epsilon+2}\,\frac{M}{d} = \frac{4\pi N\alpha_0}{3} + \frac{4\pi N}{3}\,\frac{\mu^2}{3KT+c\eta\mu^2}$$

where n = number of molecules per cc.

c = constant $\simeq$ 1.35

Wyman (121) developed an empirical equation which held surprisingly well for many liquids. Only those that were strongly associated failed to obey his equation.

This work directly led Onsager (90) to treat the subject of a cavity field which was divided into two parts. This meant that as well as a cavity field a reaction field was also present. The reaction field is produced by the action of dipoles on other dipoles. This would lead to results that are quite different from Debye's, if there were a large permanent dipole moment, and agree quite closely if only a small moment was present. By a rather rigorous mathematical treatment, which can be found in standard textbooks on dielectric theory, he obtained the equation:

$$(4)\quad \frac{\epsilon-1}{\epsilon+2}\,\frac{M}{d}-\frac{\epsilon_\infty-1}{\epsilon_\infty+2}\,\frac{M}{d}=\frac{3\epsilon(\epsilon_\infty+2)}{2\epsilon+\epsilon_\infty(\epsilon_\infty+2)}\left(\frac{4\pi N\mu_0^2}{9KT}\right)$$

Kirkwood (62)(63) extended the treatment of Onsager's equation in that he treated more accurately the existence of hindered rotation about the molecules. Kirkwood took into account forces such as Van der Waals forces and hydrogen bonding. He also eliminated the approximation of a uniform local dielectric constant. His equation was not too different from that of Onsager's except that he introduced a second dipole moment term, that of $\bar{\mu}$ which is the sum of the molecular dipole moment and the moment induced as a result of hindered rotation.

$$(5)\quad \frac{(\epsilon-1)(2\epsilon+1)}{9T}\,\frac{M}{d}=\frac{4\pi N}{3}\left(\alpha+\frac{\bar{\mu}\mu}{3KT}\right)$$

It may be shown that the Kirkwood equation is more exact than either the Debye or the Onsager equations. The Onsager equation enables one to apply calculations to the polar solvents. However, it may be concluded that the Debye equation is suitable for calculation of the static dielectric constants for gases and dilute solutions of polar solutes in non polar solvents.

From this discussion of the static dielectric constant and the equations from which it may be calculated, dielectric dispersion may now be considered.

Dielectric Dispersion

Dielectric dispersion may simply be expressed as the decrease in the dielectric constant with increasing frequency. Dispersion is the lag of the molecules resulting in the fact that they are not in equilibrium with the applied field.

The first recorded decrease in the dielectric constant with increasing frequency dates back to the nineteenth century (29).

The presently accepted viewpoint seems to be that the effect of dispersion is a result of combined orientation and distortion rather than a pure distortion of the molecules (24). The dividing line between these two effects is the relaxation time of the molecules. The relaxation time is the time required for the moments of the molecules to revert practically to a random distribution after the field has been removed. The dividing line is then expressed as $\omega \tau = 1$

where $\omega = 2\pi f$

$\tau = \dfrac{4\pi\eta a^3}{kT}$

η = viscosity

"a" = radius of molecule

It is obvious that different size molecules will have a great variety of relaxation times. Not only the size of the molecule but also the frequency and viscosity will assume important roles.

For small molecules $\tau = 10^{-11}$ sec. and for large molecules of high viscosity $\tau = 10^{-6}$ to 10^{16} sec. For polymer molecules τ shows a large range and an example of such may be shown (73):

TABLE I

Polymer	(sec)
poly(vinyl) formal	10^{16}
" acetal	10^{6}
" acetate	1.5×10^{-9}
" hexanol	4×10^{1}

If dielectric dispersion is considered, one must take into account the Brownian movement. By differentiating the Debye equation (1) one obtains:

$$(6)\quad P(\omega) = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{M}{d} = \frac{4\pi N}{3}\left[\alpha_0 + \frac{\mu^2}{3kT}\left(\frac{1}{1 + i\omega\tau}\right)\right]$$

This equation then takes into account the existence of a relaxation time. Many times in actual experimental work the existence of more than one relaxation time occurs. This was, as will be remembered, a limitation of the Debye equation. The subject will be briefly discussed in a later section.

By solving equation (6) for the dielectric constant there is obtained

$$(7) \quad \epsilon = \frac{1 + \frac{2d}{m} P(\omega)}{1 - \frac{d}{m} P(\omega)}$$

If boundary conditions are imposed, that is:

$$\omega \approx 0 ; \quad \epsilon_0 = \epsilon$$

$$\omega \approx \infty ; \quad \epsilon_\infty = \epsilon$$

and these conditions are substituted in equation (6) at both low frequencies (8a) and high frequencies (8b) then:

$$(8a) \quad P(\omega) = \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \frac{m}{d} = \frac{4\pi}{3} N \left(\alpha_0 + \frac{\mu^2}{3KT} \right)$$

$$(8b) \quad P(\omega) = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \frac{m}{d} = \frac{4\pi}{3} N \alpha_0$$

It is then possible to write the expression:

$$(9) \quad \frac{4\pi}{3} N \frac{\mu^2}{3KT} = \left[\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right] \frac{m}{d}$$

If equations (8a) and (8b) are substituted in (6) and equation (9) in (7) then an expression is obtained that will enable one to obtain the dielectric constant in expanded form.

$$(10)\ P(\omega) = \frac{m}{d}\left[\frac{(\epsilon_\infty-1)}{(\epsilon_\infty+2)} + \frac{1}{1+i\omega\tau}\left(\frac{\epsilon_0-1}{\epsilon_0+2} - \frac{\epsilon_\infty-1}{\epsilon_\infty+2}\right)\right]$$

$$(11)\ \epsilon = \frac{\dfrac{\epsilon_0}{\epsilon_0+2} + i\omega\tau\dfrac{\epsilon_\infty}{\epsilon_\infty+2}}{\dfrac{1}{\epsilon_0+2} + i\omega\tau\dfrac{1}{\epsilon_0+2}}$$

The real and imaginary components of equation (11) may be separated by mathematical manipulation.

$$(12)\quad \epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1+x^2}$$

$$(13)\quad \epsilon'' = \frac{\epsilon_0 - \epsilon_\infty}{1+x^2}$$

where $x = \dfrac{\epsilon_0+2}{\epsilon_\infty+2}\ \omega\tau$

These equations (12)(13) were modified to a slightly simple form by Frohlich.

$$(14)\quad \epsilon' = \epsilon_\infty + \frac{\epsilon_0 + \epsilon_\infty}{1+\omega^2\tau^2}$$

$$(15)\quad \epsilon'' = \frac{\epsilon_0 - \epsilon_\infty\omega\tau}{1+\omega^2\tau^2}$$

where $\epsilon_0 - \epsilon_\infty <<< 1$ and $\epsilon = \epsilon' - i\,\epsilon''$

Equation (14) required that ϵ' decrease from ϵ_0 to ϵ_∞ with an increase in frequency. In the same frequency range ϵ'' must increase from a small value through a maximum to a small value. Many liquids (Figure 2) below conform to these curves.

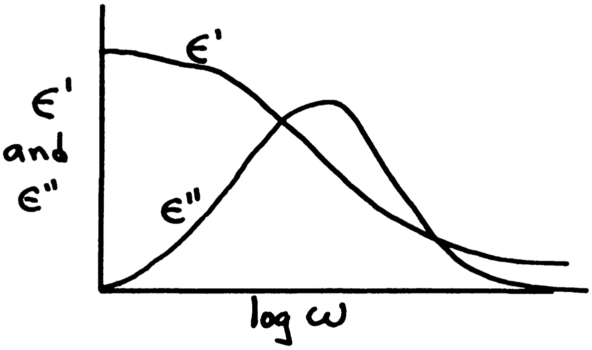
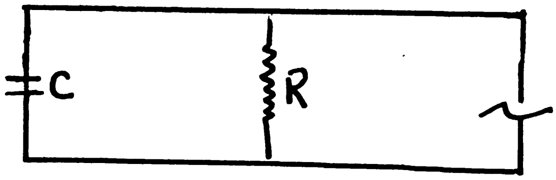


Figure 2

The relaxation time, as before explained, may be evaluated from the maximum slope of the ϵ' or the maximum value of ϵ''.

The above mathematical treatment may be further shown by an actual case of a capacitor "C" with a resistor "R".



The capacity will decrease from a large value to a small value while the resistance will decrease from an extremely large value to a small value and again increase to a large value. This behavior is perfectly analogous to that of the ϵ' and ϵ''.

An illustrative example would be that of polymer molecules in a suitable solvent. If a polymer solution is placed in a direct current field, the molecules will orientate themselves with respect to the field. This orientation cannot be perfect due to thermal motion and entanglement but the resultant orientation will be an average value. Before the field was applied the moments of the molecules were completely random. If the field is removed, the molecules will revert to their original randomness. The time for such reversion to take place has previously been defined as the relaxation time.

What would be the result should an alternating field be applied in place of the direct current field considered above? In a low frequency field the period is generally large compared to that of the relaxation time. This being true, the molecules present should have sufficient time to align and realign themselves with the field during each cycle. The dielectric constant must then remain large, ϵ_0 . As the frequency is increased a point will be reached where the orientation lags behind the reversals of the field and thus the dielectric constant decreases below ϵ_0 . The lag produced will be the greatest when the period of the frequency is of the same order as the relaxation time.

There is present at the same time a component of the total current which is in phase with the field. This, in phase, component represents a consumption of power by the dielectric. It will increase up to a point where the frequency and the relaxation time are the same, and at this frequency the ϵ'' will be at its maximum.

As the frequency is increased still further additional molecules will be unable to follow the field, and a frequency will be reached where none can follow. At this point the ϵ' decreases from ϵ_0 to ϵ_∞. At the same time ϵ'' has gone from a low value at low frequencies through a maximum at $\omega\tau = 1$ and back to a low value at high frequencies.

It seems plausible to state that the long molecules should be the first to drop out, not being able to follow the field due to the viscous drag of the environment. The shortest should be the last to drop out. This should then enable one to obtain a distribution of chain lengths as well as an excellent measure of molecular weight from this dielectric dispersion.

Methods of Measurement

The usual methods in use today for the measurement of dielectric constant and dielectric dispersion are arranged in five groups. In general they may be grouped as (1) bridge methods, (2) resonance methods, (3) force methods, (4) calorimetric methods, and (5) comparison methods.

The bridge method is the most generally useful method. The principle on which this method is based is that the voltage between two corners of the bridge is brought to zero by the adjustment of capacity and resistance. This balance occurs when the ratio of the impedances of two adjacent bridge arms is equal to the ratio of the impedances of the other pair of adjacent arms. Possibly the outstanding feature of the bridge method is its versatility.

With the bridge method a great many variations may be used: (1) substitution method, (2) direct method, and (3) parallel resistance method. A diagram of the bridge described above may be seen in the experimental section of this work (104).

Much work has been published using bridge methods or variations thereof (15)(20)(39)(43)(54)(70)(86)(87).

The resonance method of measurement is applicable over the frequency range of 100 Kc to 30 Mc. Such measurements are made by using a high frequency alternating current set up in a primary circuit. This circuit is loosely coupled to a secondary circuit containing capacitance and inductance (Figure 3).

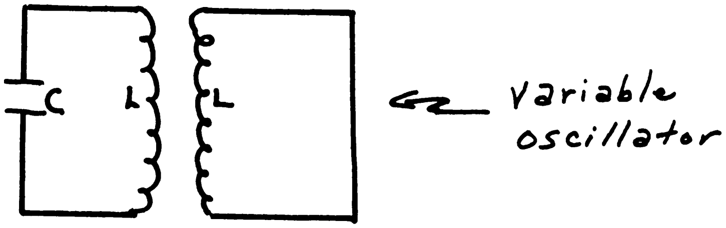


Figure 3

The frequency at which maximum voltage occurs is known as the resonance frequency and may be related to the inductance and capacity by

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

This measurement has been applied to many determinations of dielectric constant (11)(20)(32)(122) and dielectric dispersion (115).

A balance is obtained by adjusting the capacity in the secondary circuit until the current is at a maximum. The cell to be measured is then placed in parallel with the capacitor which is lowered until the voltage is again a maximum. The difference then in the condenser readings is the capacitance of the cell. The power loss may be ascertained from the width of the curve in voltage versus frequency plots. Some typical resonance circuits may be found in the references (9)(32)(122).

The force method involves the deflecting force exerted by an applied electric field upon a conducting ellipsoid suspended in solution (88).

Calorimetric methods are applicable only to the measurement of dielectric dispersion but can be used over the entire frequency range. The voltage across a cell, closed except for a small capillary tube, is carefully regulated. The solvent expands into the capillary tube as a measure of the energy absorption (25)(76)(78)(101).

Comparison methods involve the comparison of magnitude and phase of voltage across an unknown and standard capacitance. An oscilloscope is used as the means of comparison (16)(123).

Phase compensation methods are used in many instances especially for micro amounts of sample. The difference in phase is compensated by the use of a variable precision condenser (59).

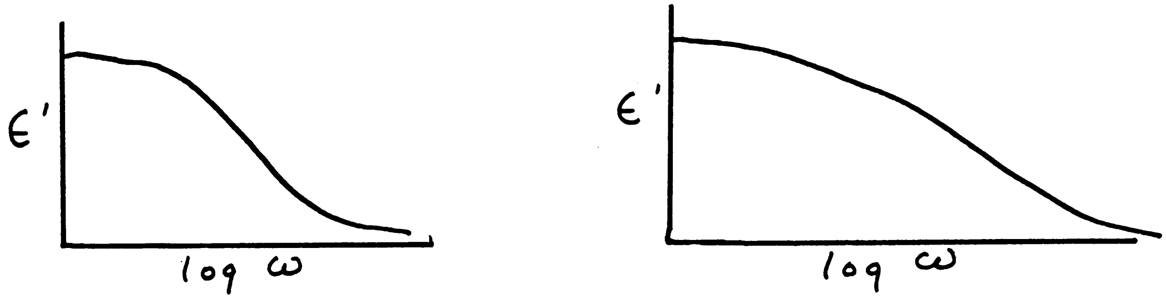
Swinging pendulum methods, cavity resonance methods, cavity perturbation methods, and heterodyne beat methods are described in the literature (17)(36)(55)(117).

There are many different types of capacitance cells. Each investigator uses one of his own choosing, each serving the one specific purpose but also presenting special features.

Presence of More Than One Relaxation Time

Debye treated molecules as spherical and thus the molecules had a single relaxation time. In reality, molecules are of many sizes and thus multiple relaxation times so that a distribution of relaxation times would then be expected.

Multiple relaxation times may be clearly shown with the use of plots of ϵ' and ϵ'' versus log ω.



(a) Actual Debye (b) Multiple relaxation

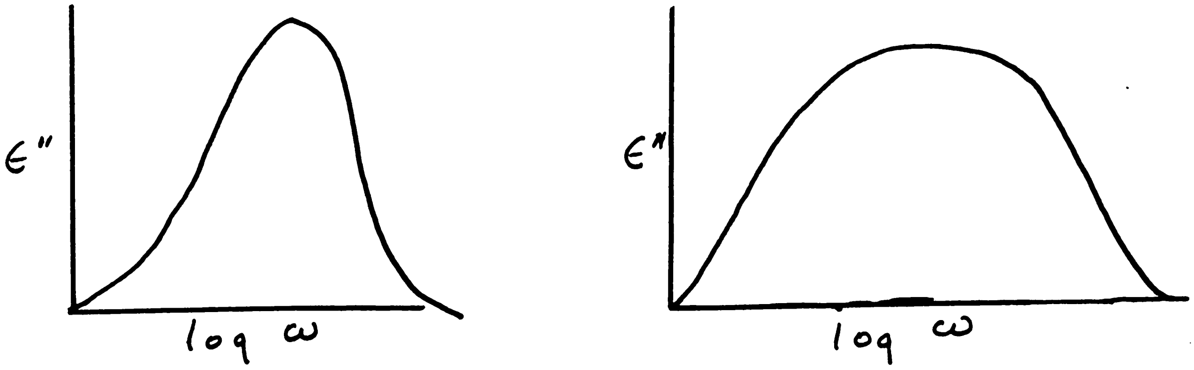


Figure 4

Equation (1) has been treated by Perrin and $\mu^2/(1+i\omega\tau)$ has been replaced by

$$\frac{\mu_1^2}{1+i\omega\tau} + \frac{\mu_2^2}{1+i\omega\tau} + \frac{\mu_3^2}{1+i\omega\tau}$$

Cole and Cole (13) developed an empirical equation which tended to explain multiple relaxation times.

$$(16)\quad \epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1+(i\omega\tau_0)^{1-\alpha}}$$

where ϵ^* = complex dielectric constant

τ_0 = most probable relaxation time

α = an empirical constant with values from 0 to 1.

This equation on separation of the real and imaginary components results in (17) and (18):

$$(17)\quad \epsilon' - \epsilon_\infty = \frac{(\epsilon_0-\epsilon_\infty)[(1+\omega\tau_0)^{1-\alpha}\sin(\alpha\pi/2)]}{1+2(\omega\tau_0)^{1-\alpha}\sin(\alpha\pi/2+(\omega\tau_0)^{2(1-\alpha)}}$$

$$(18)\quad \epsilon'' = \frac{(\epsilon_0-\epsilon_\infty)(\omega\tau_0)^{1-\alpha}\cos(\alpha\pi/2)}{1+2(\omega\tau_0)^{1-\alpha}\sin\alpha\pi/2)+(\omega\tau_0)^{2(1-\alpha)}}$$

When α = 0 the equation would reduce to the simple Debye equation. When α = 1 a uniform distribution of relaxation times is present.

If the Debye equation be combined and written in the form of the equation for a circle, $\left(\epsilon' - \frac{\epsilon_0 + \epsilon_\infty}{2}\right)^2 + \epsilon''^2 = \left(\frac{\epsilon_0 - \epsilon_\infty}{2}\right)^2$

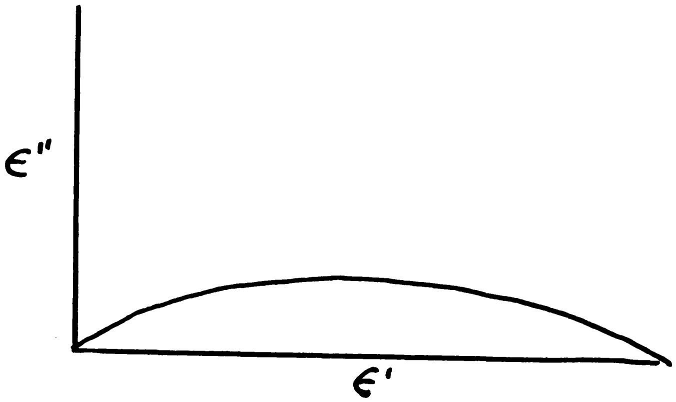


Figure 5

it can be seen that only one relaxation time is present. The plot will be that of a semicircle (49). If an arc results, then a distribution of relaxation times is present, and as the distribution becomes greater, the line will move toward the axis (73).

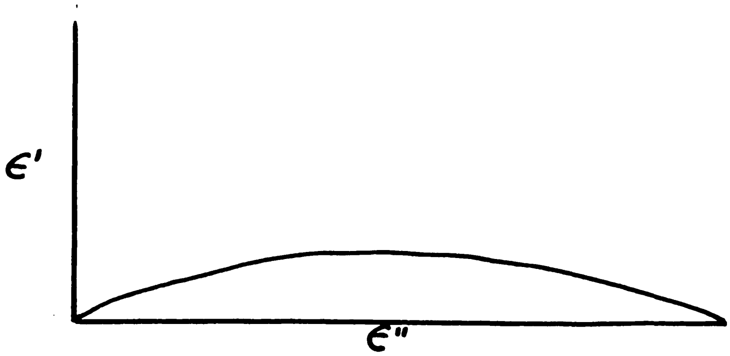


Figure 6

The relaxation time can be calculated and a complete discussion of such is given in Smyth (104).

Experimental Work on Dielectric Dispersion

In the chemical journals there appears a large volume of experimental work concerned with dielectric dispersion and loss. The great majority of such deals with high frequency measurements as well as work on solid polymers. This is very useful, however, since it leads to an understanding of the chemical nature of molecules. Much work has also been done with different classes of polymers such as cellulosics, polyvinyls, etc.

The work reported here deals exclusively with polymer solutions at low frequencies. Some work will be shown in this section that deals with all aspects of dielectric dispersion and loss.

Girard, Abadie and Charbonniere (42) investigated solid poly(vinyl chloride) with regard to the identification, not the determination, of the average degree of polymerization. By a fractionation procedure sharp fractions of molecular weight 23,000, 40,000, 72,000 and 125,000 were isolated. The lower the D.P. the lower the junction occurring between the loss curves and ionic loss curves.

Dielectric losses in solid poly(methyl methacrylate) were studied as a function of the temperature. The low temperature peak in the loss curves was believed due to a movement of the side radicals which included the $O:C-COCH_2$ groups. The movement of the polar groups in the chains tended to explain the high quality of the polymer as a glass (82).

C. P. Smyth (104) investigated solid long chain fatty acid esters of palmitic and stearic acids. From results obtained it was postulated that long chain molecules orient as a whole by rotation about the chain axis. Different isomers were found to behave quite differently in their orientational freedom. These conclusions were obtained from dielectric dispersion and loss measurements (19).

Investigations by Offengeld (84) on alkyl poly(methacrylates) were concerned with the glass temperature, Tg. Methyl showed a dispersion region below Tg where ethyl, n-butyl, and isobutyl appeared in the transition temperature. These results were confirmed by other investigators (27).

Voet (120) found for polystyrene in toluene that as the concentration was increased, the dielectric constant remained essentially the same as that of the toluene until a critical concentration was reached. At concentrations above this value the dielectric constant rose rapidly in a linear fashion to a point much too high even for the dielectric constant of the solid polymers.

Debye and Bueche (26) investigated the same system and observed no such effect for pure polystyrene-toluene systems. If a small amount of methanol was added, an effect similar to a critical concentration was observed. The results of Voet were thus attributed to experimental difficulties.

Hammerle and Kirkwood (44) modified the Kirkwood-Fuoss theory of dielectric phenomena to include hydrodynamic interactions as well as a method of root-mean-square dimensions which agreed with those obtained from light scattering and viscosity.

Another article by the above two authors (45) showed that the square root of the molecular weight is not inversely proportional to the frequency of maximum dispersion.

Two papers by Strella and Zand (112)(113) on poly(ethyl methacrylate) and poly(n-butyl methacrylate) studied dielectric properties as a means of arriving at molecular structure. Two transition regions were found. These regions were further apart in temperature in the n-butyl polymer. The ethyl polymer chain appeared stiffer than the butyl. Furthermore, a marked dependence of the relaxation time on temperature was noted in both polymer samples.

Poly(methyl methacrylate) was also investigated experimentally in order to ascertain the dependence of the dielectric constant on the absorption of water (95). It was determined that low temperature absorption could be induced by storing over water or immersing the sample in water. This would seem to account for the γ transition occasionally found in methacrylate polymers.

Erbring and Takei (33) found that polarization decreases with concentration in studying cellulose acetate in dioxane. This was due to the formation of associated compounds. In methyl alcohol - Me_2CO mixtures the polarization is constant. No reasonable explanation for such phenomena could be offered except that chemical and physical properties must be considered in dioxane.

Funt and Mason (37) investigated poly(vinyl acetate) in toluene. The molecular weights ranged from 15,000 to 100,000 and the frequency range covered 1.5 Mc to 10 Mc. A narrow range of relaxation times was found and was only a qualitative agreement with the Debye Theory. The discrepancies seem to be that absorption curves increased with increasing frequency. Dipole moments were calculated from dispersion and loss measurements.

Dielectric constants of rubber-like materials were measured over a wide frequency range and they were in agreement with the theory of Fuoss and Kirkwood. They did not show agreement with the theory of Debye due to a wide distribution of relaxation times (11).

Terylene (94) was found to possess three different and distinct dispersion regions. The first is related to the relaxation of the dipoles in the main polymer chain. The second was attributed to the presence of OH groups, and the third was associated with the conduction of charge through the material.

Abadie and coworkers (1) investigated the effect of temperature on dielectric loss with cellulose and starch. It was found as the temperature was increased the dielectric loss increased. The increase in temperature seemed to influence the environment through which the chain rotated. Measurements were made from 100 ~ to 100 Mc. The critical frequencies shifted from 800 Kc to 10 Mc.

Poly(methyl methacrylate) in toluene (21) was investigated and it was found that the dielectric constant varied with concentration. The molecular weights varied from 209,000 to 1,750,000. It was also found that the dipole moments calculated from measurements made were related to the molecular weight as was predicted by Kuhn.

Poly(methyl methacrylate) was even more thoroughly investigated as far as dielectric constant and loss was concerned (22). Molecular weights ranged from 14,000 to 1,750,000 and the solvents used were benzene and toluene. Frequency range was 10 Kc to 35 Mc and measurements were made at temperatures ranging from -30°C to 25°C. By investigation it was proven that the static dielectric constant was independent of molecular weight for a given concentration. It was also found that the dipole moment was proportional to the square root of the molecular weight. The most striking result was the fact that it claimed the molecular weight was independent of the critical frequency (fc). From results given below this does not seem to be entirely the case:

M.W.	fc
1,750,000	4.2
1,250,000	4.5
917,000	6.7
500,000	7.0
95,000	8.0
14,000	8.6

TABLE II

Brouchere and Beek (23) found for polyvinyl acetate in toluene that the square root of the molecular weight was proportional to the dipole moment. The dipole moment was also found to be directly proportional to the root-mean-square end to end distance. They discovered, as was also claimed in the above paragraph, that the critical frequency was independent of molecular weight. This is a direct contradiction of Kirkwood-Fuoss theory (64), Kuhn's theory and the author's Master of Science thesis. It was claimed that the deviation could be explained by the simple model used by Bueche and by Rouse. The authors of this work made the suggestion that new experimental work be carried out to see if these results were correct. In both of the preceding articles the claim of no dependence of critical frequency is possibly due to two conditions. The first is that the frequency region is too high for a molecular weight dependent region and also in many cases the result is obscured by the combination of two or more dispersion regions.

Kirkwood and Fuoss (64) treated in a theoretical manner the relationship of relaxation time to the distribution of chain lengths. It was found to be a direct proportionality.

Testerman (100) found agreement with resonance absorption but not of the Debye type in the frequency range studied. Nitrocellulose was measured in acetone from 100 Kc to 500 KC, and a resonance method using substitution methods was employed. A loosely held random coil was postulated and a direct correlation was found between distribution curves obtained by fractional precipitation.

Pauley and Testerman (92) found that Testerman's dispersion (100) was due to a copper-cellulose nitrate complex. The dielectric dispersion is due to the formation of polymer aggregates due to crosslinking of polymer molecules. As with Testerman's work, it would seem that the dispersion region observed was a secondary region and not that of a primary nature. The region observed was so narrow that it was not likely to be anything but rotation of side chains or possibly a longitudinal spinning.

In the author's Master of Science work 5% solutions of cellulose acetate in dioxane were measured from 50 cycles to 5 Mc by a bridge method. A dispersion region was observed from which the critical frequency could be obtained. The critical frequency is the frequency where the dispersion is 50% complete. The critical frequency could be related to the degree of polymerization through an empirical correlation.

$$\log \text{D.P.} = 2.60 - .67 \log (\nu_c + 1)$$

where ν_c = critical frequency

Molecular weights can be calculated in record time. The present work is a continuation of such studies on ethyl cellulose fractions.

The references contained in this section are only a minute fraction of work done, but it is hoped that it will give an idea of the many different viewpoints as well as information that can be obtained concerning chemical structure.

EXPERIMENTAL

EXPERIMENTAL EQUIPMENT, PROCEDURE, AND RESULTS

Materials Used

The ethyl cellulose used throughout this investigation was a commercial grade obtained from Hercules Powder Company of Wilmington, Delaware.

Grade	Ethoxy Content	Viscosity
N-200	48.7%	169 centipoises in 5.0% solution

The acetone, C. P., was obtained from Commercial Solvents Corporation of Newark, New Jersey.

Ethyl acetate was also obtained from Commercial Solvents Corporation and was commercial grade.

Dioxane, purified grade, was obtained from Fisher Scientific Company, Fair Lawn, New Jersey.

Benzene was also obtained from Fisher Scientific Company and was certified grade.

Carbon tetrachloride, certified grade, was obtained from Fisher Scientific Company, Fair Lawn, New Jersey.

Normal butyl acetate also was obtained from Fisher Scientific Company and was certified grade.

The toluene used in this investigation was obtained from Baker Chemical Company of Phillipsburg, New Jersey, and and was certified grade.

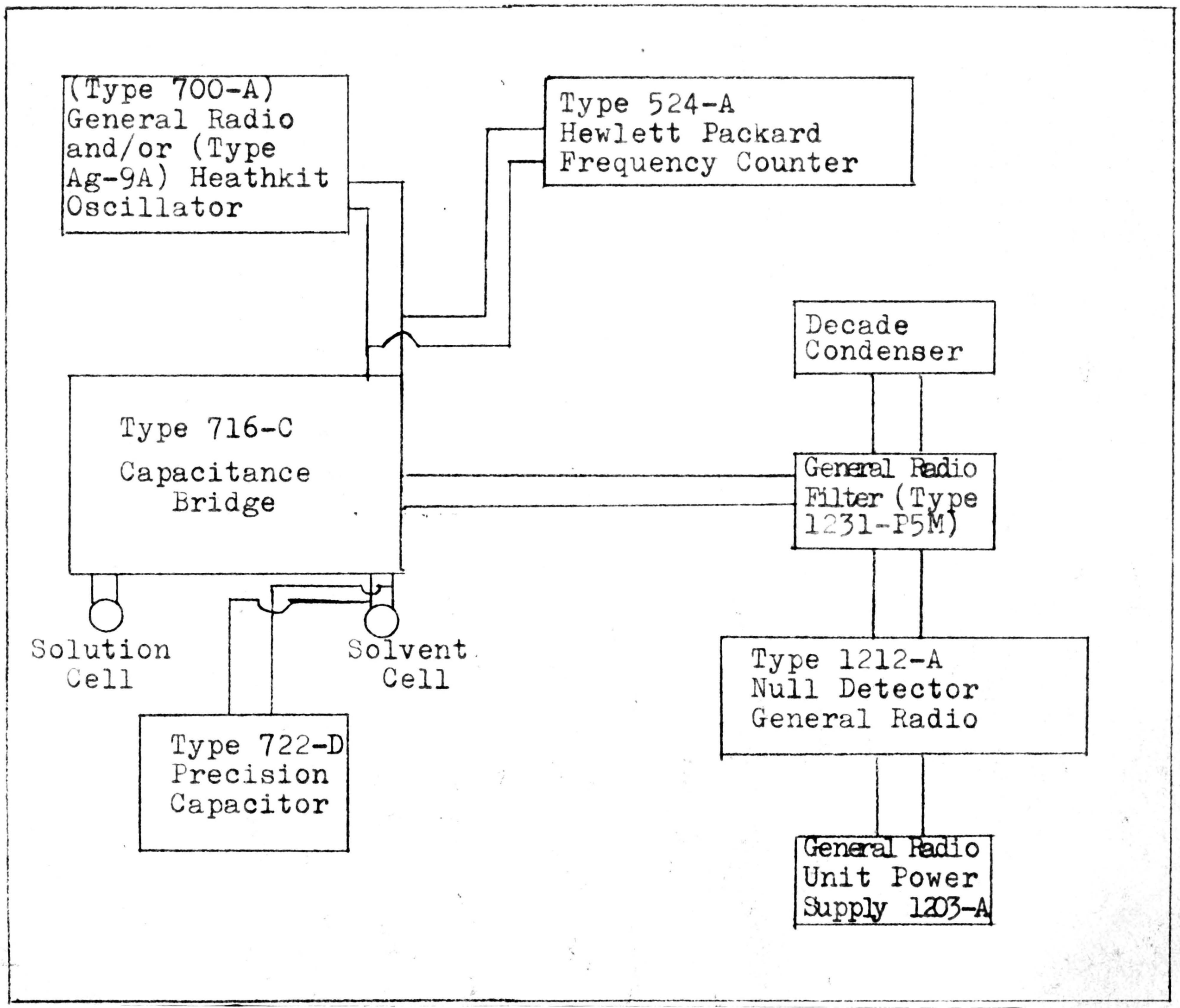
Apparatus

Essentially the same apparatus was used in this investigation as was used in the author's Master of Science thesis with slight modifications and additions. The bridge method was used due to its applicability at low frequencies and the precision that could be obtained. A block diagram of the apparatus may be seen in Figure 7 as well as a photograph of the apparatus as it stood.

The main components of the pictured apparatus were (A) two variable oscillators, (B) frequency counter, (C) capacitance bridge, (D) variable precision capacitor, (E) null detector, (F) unit power supply, (G) filter, (H) decade capacitor, and (I) two capacitance cells.

The Heathkit oscillator (A) was used from 10 cycles to 100 kilocycles due to the absence in it of hum which was found present in the General Radio oscillator. The model AG-9A Heathkit has low distortion signals over the frequency range. The other variable oscillator (A) was manufactured by General Radio Company and was type 700-A. It was used over the frequency range of 100 kilocycles to 400 kilocycles. It consists of two high frequency oscillators, one fixed and the other variable. It feeds a detector from which the different frequencies are obtained. The frequency ranges from 50 cycles to 5 megacycles. A vacuum-tube voltmeter is used in the oscillator for a measure of the output voltage.

FIGURE 7. BLOCK DIAGRAM OF APPARATUS



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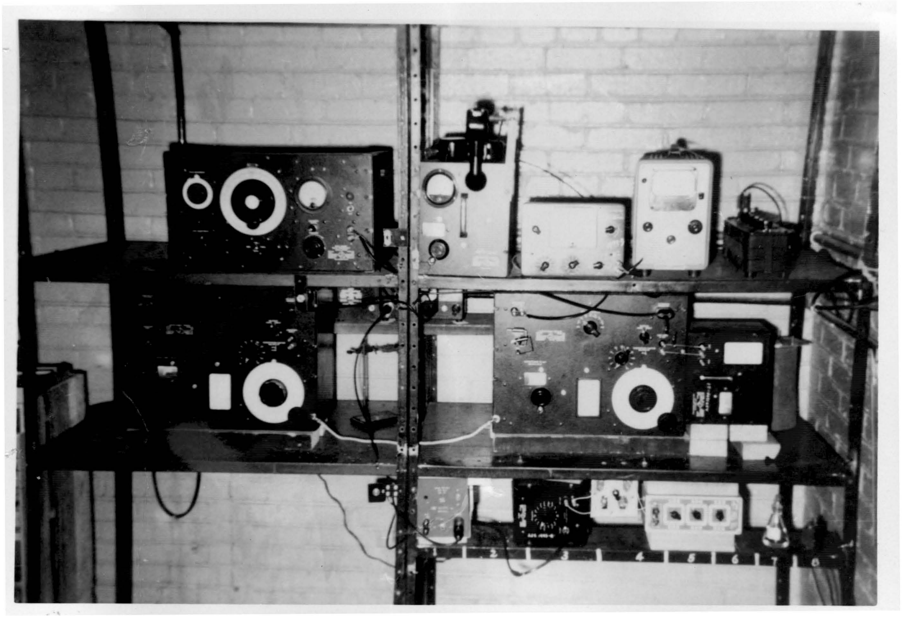


The frequency counter (B) was manufactured by the Hewlett-Packard Company and is type 524-A. It can be used to count frequency from 10 cycles per second to 10 megacycles per second. The counter has an accuracy of 0.03%. The meter has a crystal oven, as well as a fan for temperature control. It is possible to hold the count for both long or short periods.

The capacitance bridge (C) was manufactured by General Radio Company and is type 716-C. It is a modified Schering bridge with direct reading in capacitance at any frequency. It may be used to measure dissipation-factor, dielectric constant, as well as dielectric properties. The bridge is capable of measurements by a direct method, a substitution method, and a parallel resistance method. Variations of temperature over the normal range have no effect on the accuracy of the bridge.

The variable precision capacitance (D) was manufactured by General Radio Company and is type 722-D. It has the features of high stability, high precision of setting (1 part in 25,000 of the full scale), low backlash, and low dielectric losses. It has an accuracy of ±0.1%.

The null detector (E) was manufactured by General Radio Company and is type 1212-A. It is designed primarily as a balance-indicator in A-C bridge measurements. It consists of a 3-stage broad-band amplifier with series-peaking compensation. This null detector has a sensitivity of approximately 40 microvolts.

The unit power supply (F) was also manufactured by General Radio Company and is type 1203-A. It is connected with the null detector by a multipoint connector.

The filter (G) was manufactured by General Radio Company and is of the type 1231-P5M. It is used to reduce harmonics and may be set to any frequency between 100 cycles and 400 kilocycles by the use of an external capacity box and inductor box.

The decade capacitor (H) was manufactured by Electronic Instrument Company and any capacity between 0.1 microfarads and .001 microfarads may be obtained.

The capacitance cells (I) were manufactured by J. C. Balsbaugh and consist of three concentric nickel cylinders. They give a nominal air capacity of 100 micro microfarads.

The chassis was connected to earth ground and all leads between components were shielded.

Refractionation of Ethyl Cellulose Fractions

Fractions obtained by McNeer (80) were carefully refractionated in order to obtain as sharp fractions as possible in the following manner. The refractionation procedure was one developed by McNeer and modified slightly by the author.

Fifty grams of ethyl cellulose were dissolved in 1910 grams of ethyl acetate and the solution was stored at 25.0°C for 24 hours. This waiting period insured a homogeneous swelling of the ethyl cellulose by the ethyl acetate. The addition of

7640 grams of acetone was then made which dissolved the gel formed by the previous addition, resulting in a one-half percent solution. This low concentration was used to insure a precision fractionation. The solution was well agitated until complete solution had been accomplished and again allowed to stand at 25.0°C for at least four hours.

Non solvent, in the ratio of 95:5 water-acetone, was slowly added until a slight local precipitation took place. This precipitation was indicated by an increased turbidity. The solution was slowly agitated until the precipitation had disappeared and was then allowed to stand an additional hour at 25.0°C, and then placed in a 15.0°C room for a period of 18 hours.

The first fraction appeared at the bottom of a 20 liter pyrex bottle in the form of a hard gel. The gel was then separated from the solution by decantation into another 20 liter bottle. The decanted solution was placed in the 25.0°C room in order to return to 25.0°C. The non solvent was then added as above described and another gel settled after 18 hours. The amount of non solvent varied for each addition. In most cases the addition of non solvent was increased for each fraction.

The gel was recovered in each case by dissolving it in a minimum amount of acetone. This led to a very viscous syrup which was then added slowly to large amounts of distilled water. This precipitated the polymer into a fibrous material which was filtered, dried, and then stored away from direct light. If the dissolved gel was very fluid, it could be recovered by evaporation of acetone.

The specific viscosity of each recovered fraction was determined, and any fractions with similar values were recombined and refractionated according to the above procedure.

The weight and degree of polymerization of the fractions obtained are listed in Table III.

Weight and D.P. of Ethyl Cellulose Fractions

Fraction No.	D. P.	Weight (grams)
1	295	22
2	170	2
3	155	2
4	140	9
5	120	33
6	100	66
7	87	4.5
8	75	43
9	50	3

TABLE III

Intrinsic Viscosity of Ethyl Cellulose Fractions

In the determination of intrinsic viscosity Ostwald viscometers as well as Ubbelohde dilution viscometers were employed. The samples were prepared by drying one hour at 105.0°C and the desired amount was weighed out and dissolved in a desired solvent.

From results obtained by dielectric dispersion in various solvents it was necessary to determine intrinsic viscosities in the same solvents. For this reason results on dioxane, benzene, toluene, and carbon tetrachloride are included in Tables IV, V, VI and VII and Figures 8, 9, 10 and 11. W. C. Lawrence investigated ethyl cellulose in n-butyl acetate and the intrinsic viscosity values appear in Figure 12 and Table VIII as well as in his work (69). The least squares method was applied to each fraction.

Experimental Results of Dielectric Dispersion

Types of Bridge Measurement - As was mentioned earlier there is the possibility of using either the direct method, substitution method, or parallel resistance method. Another, not previously mentioned, is the differential method.

Direct Method - The capacitance cell is connected into the unknown direct terminals in the direct method. The method switch is set on "direct" and the range selector switch is set at the appropriate value. The ratio of f to f_o(where f is the frequency read from the frequency counter and f_o the value of the range selector dial) must not exceed a value of 3.0. For a

TABLE IV

INTRINSIC VISCOSITIES OF ETHYL CELLULOSE FRACTIONS IN DIOXANE AT 25°C

Fraction	η_{sp}/C	C(g/100 ml)	$[\eta]$(dl/g)
Original Material - 1	4.660	0.4176	2.98
	4.500	0.3862	
	4.234	0.3146	
	4.037	0.2536	
	3.747	0.1870	
	3.457	0.1268	
	3.376	0.0966	
	3.285	0.0787	
Original Material - 2	2.740	0.4580	1.93
	2.348	0.2290	
	2.191	0.1270	
	2.164	0.1145	
	2.061	0.0635	
	2.052	0.0573	

TABLE IV (Continued)

Fraction	η_{sp}/C	C(g/100 ml)	$[\eta]$ (dl/g)
F-1	4.128	0.3330	3.01
	3.764	0.2279	
	3.568	0.1614	
	3.305	0.0809	
	3.195	0.0570	
	3.119	0.0404	
F-2	3.179	0.3576	2.20
	3.085	0.3320	
	2.710	0.1788	
	2.660	0.1660	
	2.420	0.0830	
	2.329	0.0447	
F-3	3.302	0.5124	1.98
	2.938	0.3722	
	2.626	0.2562	
	2.500	0.1861	
	2.430	0.1826	
	2.300	0.1252	
	2.205	0.0913	

TABLE IV (continued)

Fraction	η_{sp}/C	C(g/100 ml)	$[\eta]$ (dl/g)
F-4	1.745	0.5432	1.18
	1.639	0.3852	
	1.544	0.3352	
	1.504	0.2716	
	1.383	0.1926	
	1.357	0.1676	
	1.259	0.0838	
F-5	1.549	0.4860	1.15
	1.507	0.4152	
	1.420	0.3116	
	1.365	0.2430	
	1.351	0.2076	
	1.276	0.1558	
	1.234	0.1038	
F-6	1.544	0.4232	1.12
	1.521	0.3776	
	1.366	0.2116	
	1.344	0.1888	
	1.209	0.1058	
	1.174	0.0529	
	1.150	0.0472	

TABLE IV (Continued)

Fraction	η_{sp}/C	C(g/100 ml)	$[\eta]$ (dl/g)
F-7	1.177	0.3976	1.00
	1.140	0.3450	
	1.081	0.1988	
	1.061	0.1725	
	1.039	0.0994	
	1.022	0.0497	
F-8	1.201	0.4764	0.92
	1.074	0.2686	
	1.055	0.2382	
	0.959	0.0672	
	0.950	0.0596	
	0.938	0.0336	
F-9	0.666	0.3970	0.63
	0.665	0.3006	
	0.658	0.1985	
	0.653	0.1503	
	0.646	0.0993	
	0.627	0.0752	
B-1	1.682	0.3962	1.41
	1.599	0.2550	
	1.577	0.1981	
	1.509	0.1275	
	1.470	0.0991	
	1.444	0.0638	

TABLE IV (Continued)

Fraction	η sp/C	C(g/100 ml)	$[\eta]$ (dl/g)
B-2	2.110	0.4730	1.54
	1.930	0.3582	
	1.840	0.2365	
	1.720	0.1577	
	1.660	0.1194	
	1.700	0.1185	
	1.610	0.0896	
B-3	2.100	0.3996	1.65
	1.900	0.2238	
	1.881	0.1998	
	1.787	0.1119	
	1.770	0.0999	
	1.714	0.0560	
B-4	3.700	0.4176	2.59
	3.502	0.3380	
	3.306	0.2750	
	3.202	0.2260	
	3.052	0.1750	
	2.863	0.1000	

TABLE V

INTRINSIC VISCOSITIES OF ETHYL CELLULOSE FRACTIONS IN BENZENE AT 25°C

Fraction	η sp/C	C(g/100 ml)	$[\eta]$(dl/g)
Original Material - 1	5.610	0.2812	3.47
	4.720	0.1662	
	4.510	0.1406	
	4.320	0.1108	
	4.060	0.0838	
	3.990	0.0703	
B-2	3.490	0.4442	1.84
	2.910	0.2961	
	2.500	0.1777	
	2.430	0.1658	
	2.310	0.1270	
	2.190	0.0947	
	2.130	0.0829	

TABLE V (continued)

Fraction	η sp/C	C(g/100 ml)	$[\eta]$(dl/g)
F-6	1.670	0.4394	1.22
	1.510	0.3046	
	1.440	0.2197	
	1.400	0.1758	
	1.360	0.1523	
	1.350	0.1255	
	1.320	0.1015	
	1.300	0.0762	
F-8	1.340	0.4904	0.99
	1.310	0.4504	
	1.220	0.3269	
	1.150	0.2252	
	1.140	0.1962	
	1.100	0.1501	
	1.060	0.1226	

TABLE VI

INTRINSIC VISCOSITIES OF ETHYL CELLULOSE FRACTIONS IN TOLUENE AT 25°C

Fraction	η_{sp}/c	C(g/100 ml)	$[\eta]$ (dl/g)
Original Material -1	5.940	0.2710	3.18
	5.000	0.1752	
	4.520	0.1355	
	4.370	0.1168	
	4.090	0.0876	
	3.850	0.0675	
B-2	3.660	0.4724	1.77
	3.080	0.3204	
	2.670	0.2362	
	2.500	0.1890	
	2.420	0.1602	
	2.300	0.1242	
	2.210	0.1050	

TABLE VI (Continued)

Fraction	η_{sp}/c	C(g/100 ml)	$[\eta]$ (dl/g)
F-5	2.170	0.4724	1.37
	2.130	0.4478	
	1.960	0.3558	
	1.750	0.2239	
	1.690	0.1779	
	1.620	0.1493	
	1.560	0.1120	
F-8	1.330	0.5046	1.02
	1.230	0.3210	
	1.170	0.2523	
	1.150	0.2140	
	1.100	0.1682	
	1.070	0.1262	

TABLE VII

INTRINSIC VISCOSITIES OF ETHYL CELLULOSE FRACTIONS IN CARBON TETRACHLORIDE AT 25°C

Fraction	η_{sp}/c	C(g/100 ml)	$[\eta]$(dl/g)
Original Material - 1	6.350	0.2834	3.49
	5.550	0.2064	
	4.900	0.1417	
	4.520	0.1032	
	4.440	0.0945	
	4.260	0.0826	
	4.180	0.0709	
B-2	3.120	0.2938	2.01
	2.700	0.1880	
	2.570	0.1469	
	2.470	0.1253	
	2.390	0.0979	
	2.320	0.0735	

TABLE VII (Continued)

Fraction	η sp/c	C(g/100 ml)	$[\eta]$ (dl/g)
F-6	2.110	0.4824	1.37
	1.930	0.3570	
	1.770	0.2766	
	1.640	0.1785	
	1.580	0.1383	
	1.560	0.1190	
	1.530	0.0893	
F-8	1.530	0.5000	1.03
	1.350	0.3180	
	1.280	0.2500	
	1.230	0.2120	
	1.200	0.1667	
	1.170	0.1250	
	1.130	0.1060	

FIGURE 8. INTRINSIC VISCOSITY OF ETHYL CELLULOSE FRACTIONS

Dioxane Solvent

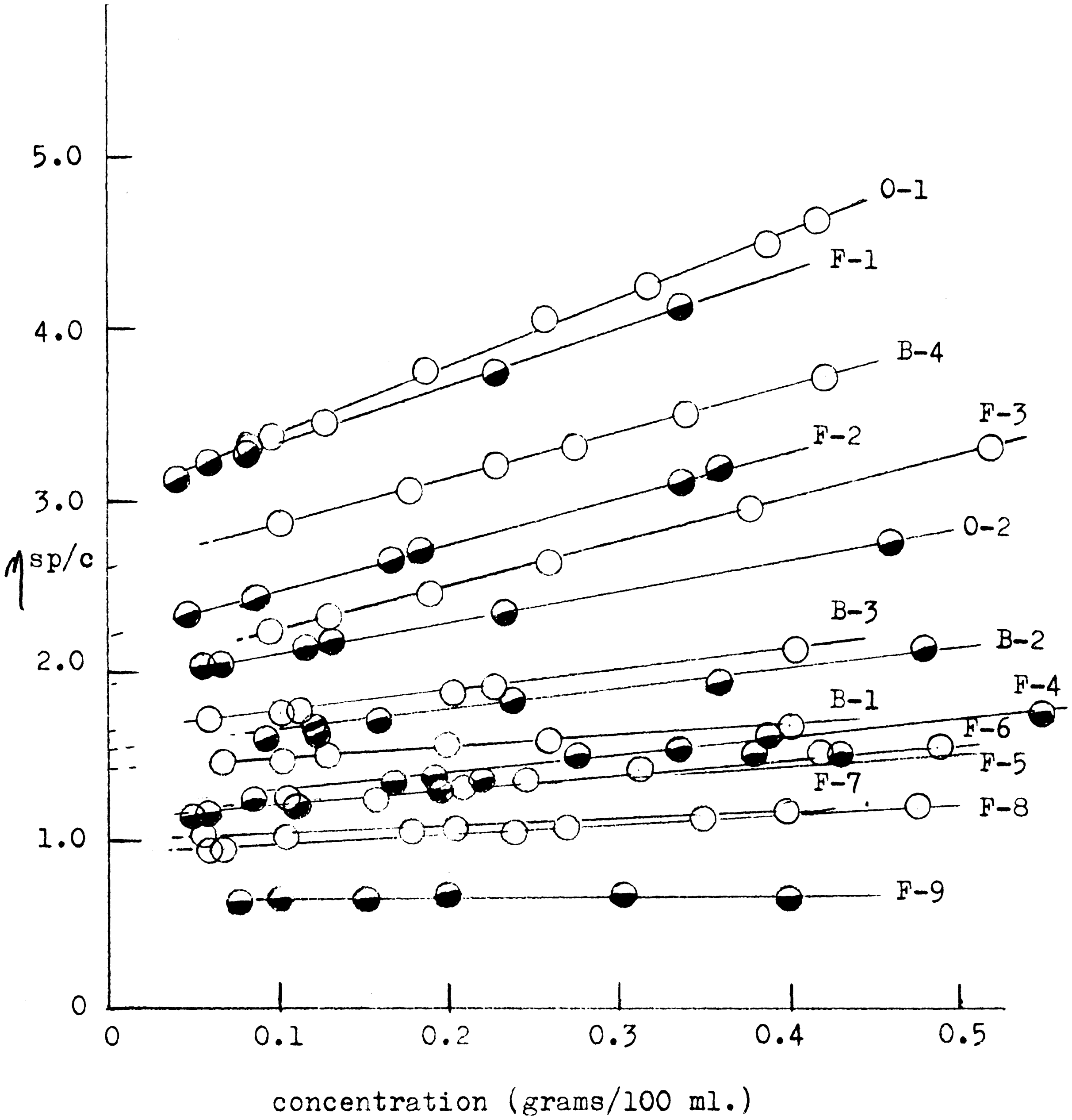


FIGURE 9. INTRINSIC VISCOSITY OF ETHYL CELLULOSE FRACTIONS

Benzene Solvent

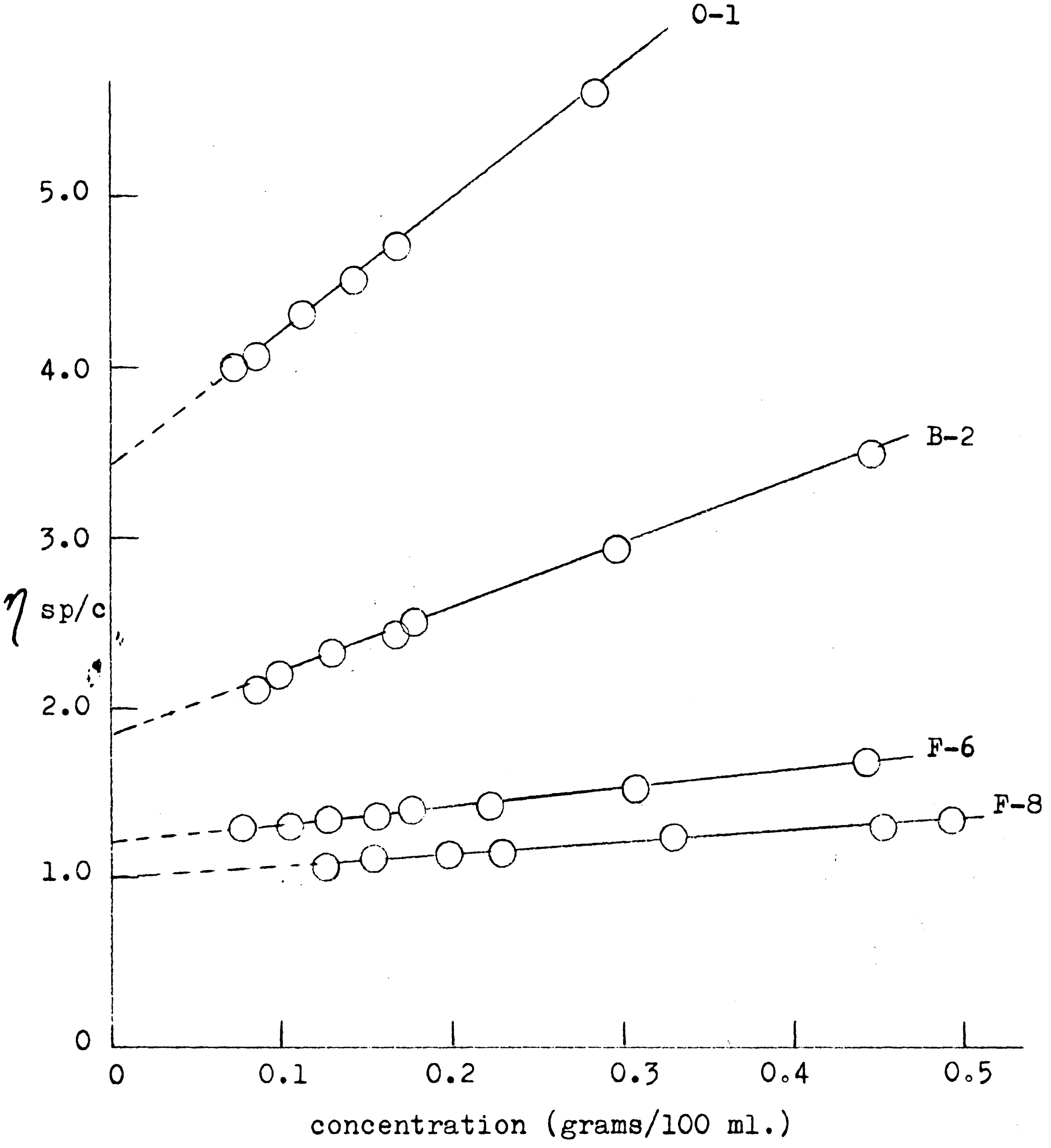


FIGURE 10. INTRINSIC VISCOSITY OF ETHYL CELLULOSE FRACTIONS
Toluene Solvent

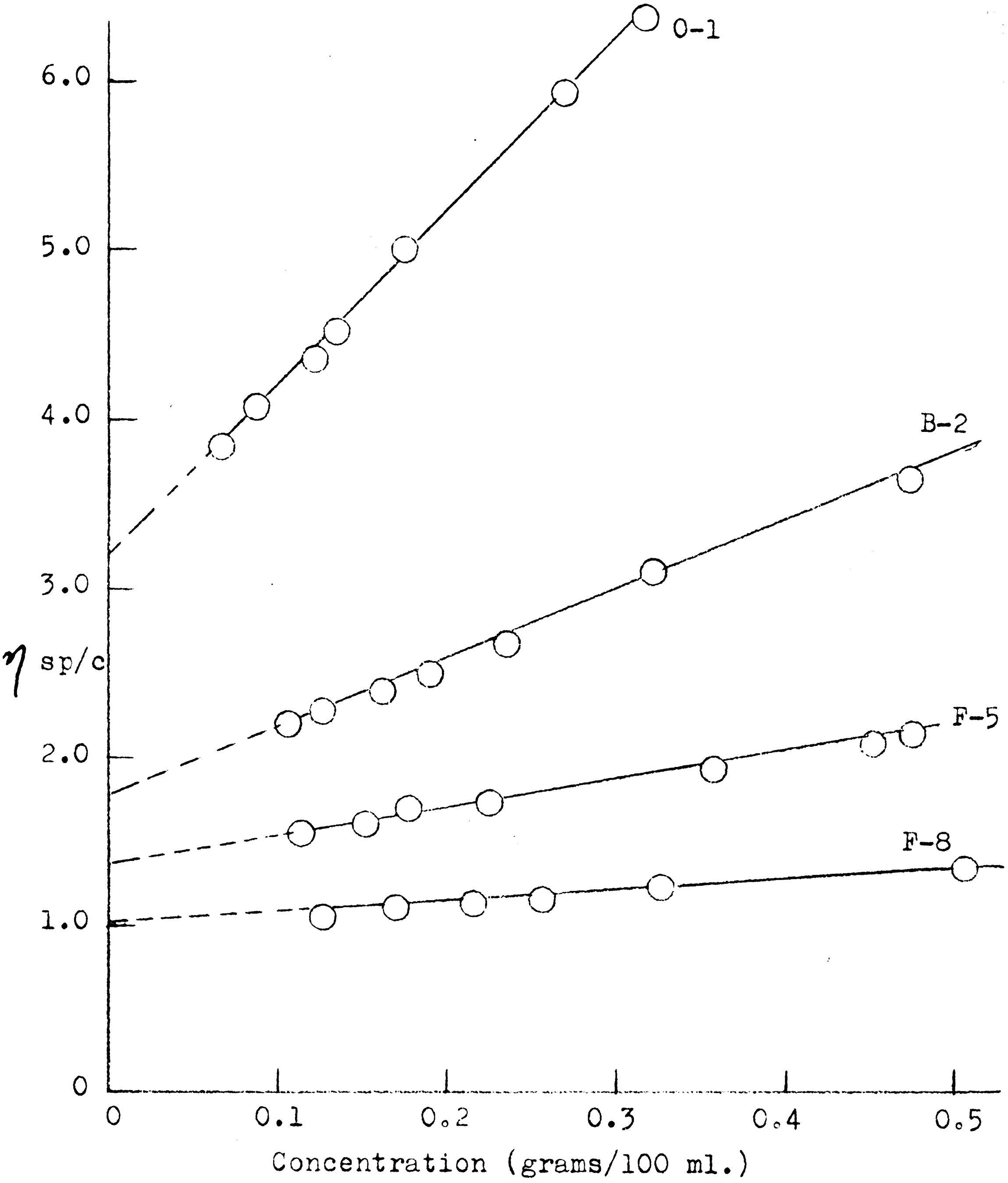


FIGURE 11. INTRINSIC VISCOSITY OF ETHYL CELLULOSE FRACTIONS

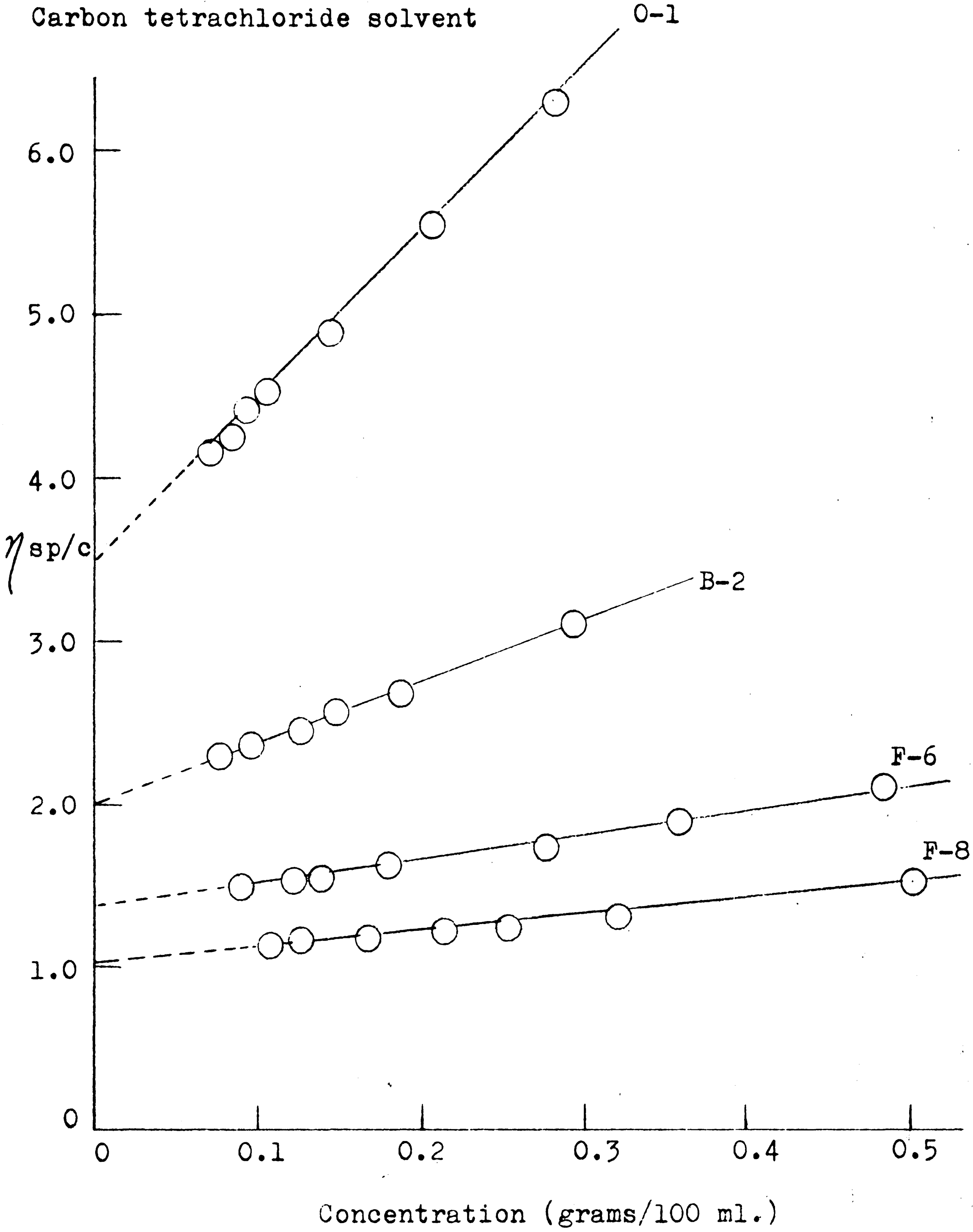


TABLE VIII

VISCOSITY OF ETHYL CELLULOSE IN n-BUTYL ACETATE

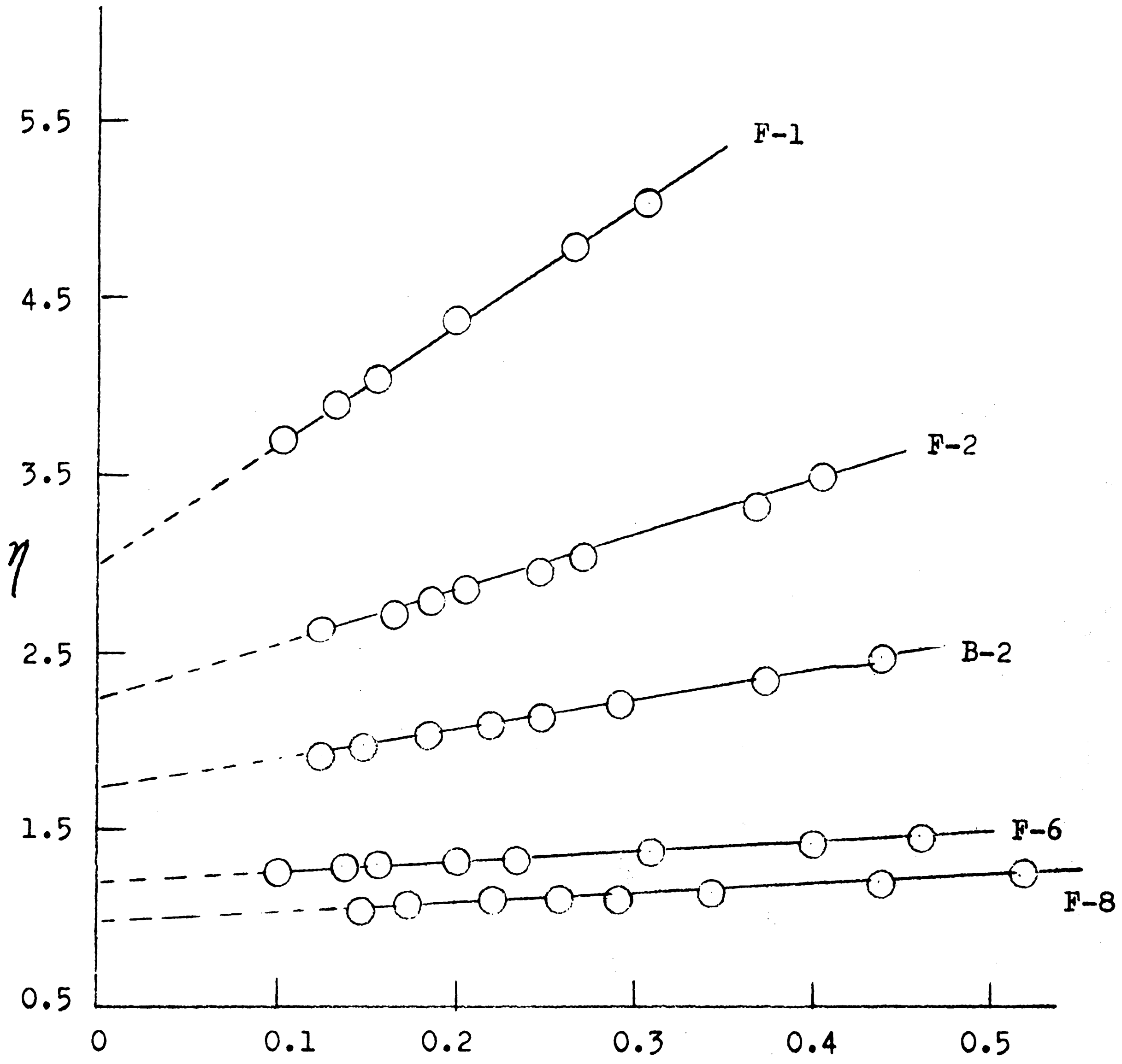
Fraction	η_{sp}/C	C(g/100 ml)	$[\eta]$ (dl/g)
F-1	5.00	0.3064	
	4.76	0.2645	
	4.36	0.1984	3.04
	3.99	0.1532	
	3.90	0.1323	
	3.70	0.1021	
F-2	3.49	0.4012	
	3.37	0.3656	
	3.05	0.2675	2.23
	2.97	0.2437	
	2.85	0.2006	
	2.80	0.1828	
	2.73	0.1605	
	2.63	0.1219	
B-2	2.48	0.4368	
	2.34	0.3678	
	2.22	0.2912	1.72
	2.13	0.2452	
	2.09	0.2184	
	2.03	0.1839	
	1.97	0.1456	
	1.93	0.1226	

TABLE VIII (Continued)

Fraction	η_{sp}/C	C(g/100ml)	$[\eta]$(dl/g)
F-6	1.47	0.4606	
	1.42	0.3986	
	1.36	0.3070	
	1.31	0.2303	1.16
	1.30	0.1993	
	1.27	0.1535	
	1.26	0.1329	
	1.23	0.0997	
F-8	1.23	0.5162	
	1.19	0.4376	
	1.15	0.3442	0.98
	1.12	0.2918	
	1.11	0.2581	
	1.09	0.2188	
	1.07	0.1721	
	1.04	0.1459	

FIGURE 12. INTRINSIC VISCOSITY OF ETHYL CELLULOSE FRACTIONS

n-Butyl Acetate Solvent



Concentration (grams/100 ml.)

balance the bridge capacitance and dissipation dials are alternately adjusted until the null has been reached; this is evidenced by a zero reading of the null detector. The bridge condenser gives the capacitance of the cell, either empty or filled with an unknown.

In cases where a solvent of high dielectric constant is under investigation, the dissipation reading is many times too high. A correction must be applied by the following equations to lower the capacitance to its true value.

$$C_{xp} = \frac{C}{1 + D_x^2} \qquad D_x = .01 \frac{f}{f_0} D$$

where D = dissipation dial reading

f = applied frequency

f_0 = value of range selector switch

C = capacitance from bridge condenser dial

Cxp = corrected capacitance

In the direct method it is also necessary to take into account the change in the bridge itself over the frequency range as well as the capacitance of the leads. These values are substracted from the bridge capacitance values. A simplified circuit diagram of the above described method is given below.

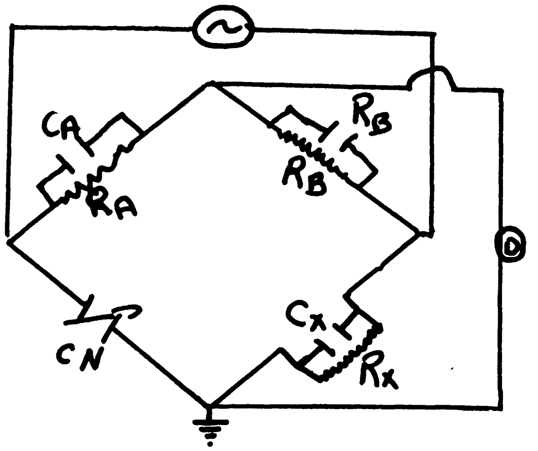


Figure 13

where ~ = oscillator

D = detector

R_A and R_B = resistance of internal ratio arms

C_A and C_B = capacitance of internal ratio arms

C_N = variable bridge condenser

C_X and R_X is capacitance and resistance of cell

Substitution Method

The substitution method employs the precision condenser, previously described. It eliminates many errors inherent in the direct method. The precision condenser is connected into the unknown direct terminals and the unknown is placed in the unknown substitution terminals. The method switch in this series is set for "substitution" and the bridge condenser is set at a fixed value. The dissipation dial and the precision condenser are then adjusted alternately, as before, until a value for the unknown is measured. A correction must be made for the dissipation factor:

$$C_{xp} = \Delta C \frac{1 - (\Delta D)^2 \frac{C}{\Delta C}}{1 + (\Delta D)^2}$$

where ΔC = C' - C

ΔD = D - D'

C' & D' = initial capacitance and dissipation reading

C & D = final capacitance and dissipation readings

Cxp = corrected capacitance

A simplified circuit diagram of the substitution method is shown below:

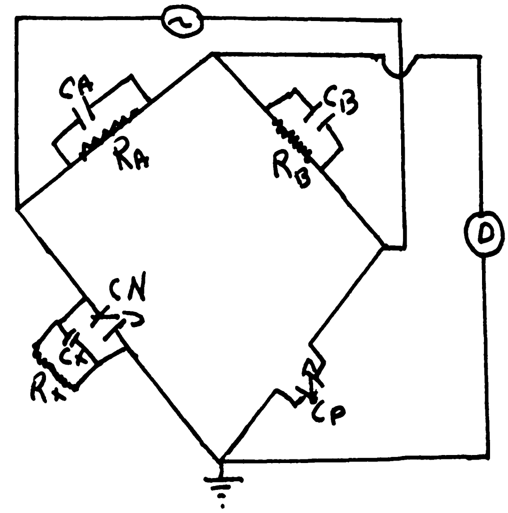


Figure 14

where symbols are the same as used in direct method

Cp = variable precision condenser

Other than the errors eliminated by this method, there appear several other very distinct advantages. In the direct method the range selector switch could not exceed a value of 3.0 for the ratio of f to f_0. In the substitution method this ratio could be extended to 10.0. This then enabled one to obtain lower dissipation readings for certain frequencies. Another distinct advantage is the ability to use the low range on the precision condenser which allows one to measure differences in capacity of .01 micro microfarads.

Parallel Resistance Method

The parallel resistance method offers a means of measuring solvents of high dielectric constant, that is, high conductivity. It is used either with the direct or substitution method. Balance is obtained in this case by alternately adjusting a decade resistor and the capacitance dials. This method presents difficulties which will be described in more detail in a later section. A diagram of the above is shown below:

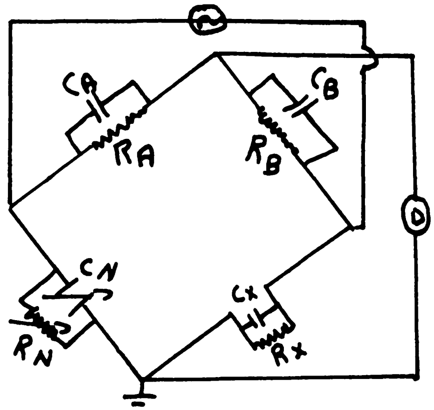


Figure 15

where symbols are same as previously described

R_N = variable decade resistor

Differential Method

The differential method is a hybrid method. It uses two cells, one on the direct side and the other on the substitution side. The cell placed on the substitution side contains the unknown solution and the cell placed on the direct side contains the solvent. It is supposed that the effect of the solvent is taken into account with each measurement. Therefore, the effect of the solute molecules is clearly shown rather than the solution as a whole. This will later be shown to be true. The balance is performed in the same fashion as either the direct or substitution method. The diagram for this method is shown below.

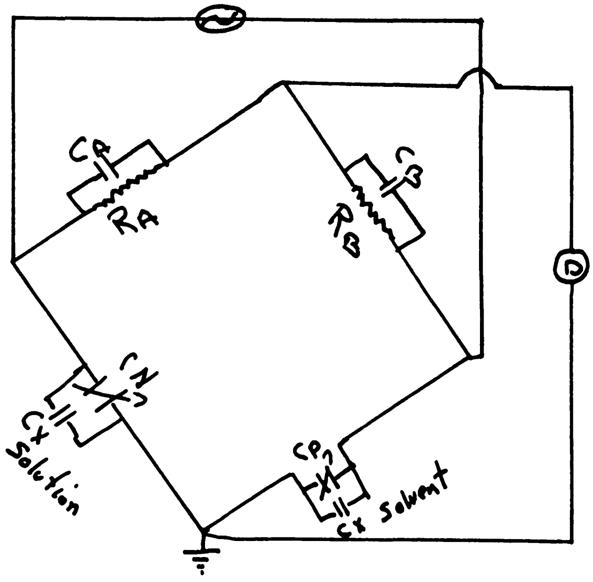


Figure 16

where symbols are same as previously described.

Preliminary Determinations - As was true with beginning work on dielectric dispersion, certain preliminary measurements must be performed. Since this work is a continuation of the author's Master of Science work, there would be no purpose in checking the operation of instruments. Dielectric constants have been determined periodically by numerous persons and this would seem to be an excellent check on the functionality of the bridge and related equipment. For this reason only certain other aspects must be checked before obtaining conclusive results.

The dispersion region was the first thing that was necessary to ascertain. With high polymer solutions there seemed to be a number of dispersion regions, all of which should not be molecular weight dependent. Only the one or ones that depended on the longitudinal dipole rotation of the polymer molecules should be molecular weight dependent. For this reason then ethyl cellulose was dissolved in a suitable solvent, in this case dioxane, and the frequency range from 300 cycles to 400 kilocycles was covered using the substitution method. In the region 300 cycles to 400 kilocycles there was only one dispersion region. At 420 kilocycles there appeared the start of a second dispersion region (Table IX).

The solvent was also run throughout this region to determine if the dispersion could be due to solvent. It was found that this was not true (Table X).

TABLE IX

Substitution Method — Ethyl Cellulose in Dioxane
F-6 0.3 grams/100 ml.

Frequency	Capacity (Cell Out)	Capacity (Cell In)	ΔC
300 cps	97.7	253.8	156.1
400 cps	97.7	253.8	156.1
600 cps	97.7	253.8	156.1
800 cps	97.7	253.8	156.1
1 kc	97.7	253.6	155.9
2 kc	97.7	253.5	155.8
3 kc	97.7	253.4	155.7
6 kc	97.7	253.3	155.6
8 kc	97.7	253.2	155.5
10 kc	97.7	253.1	155.4
15 kc	97.7	252.6	154.9
20 kc	97.6	252.4	154.8
30 kc	97.5	251.8	154.3
35 kc	97.5	251.5	154.0
40 kc	97.5	251.3	153.8
50 kc	97.5	251.0	153.5
60 kc	97.5	250.8	153.3
80 kc	97.5	250.2	152.7
100 kc	97.4	250.0	152.6
120 kc	97.4	249.7	152.3
200 kc	97.3	249.3	152.0
300 kc	97.1	249.0	151.9
400 kc	96.9	248.8	151.9
420 kc	96.8	248.2	151.4

TABLE X

Substitution Method Dioxane Solvent

Frequency	Capacity (Cell In)	Capacity (Cell Out)	ΔC
400 cps	744.5	497.7	246.8
500 cps	744.5	497.7	246.8
600 cps	744.5	497.7	246.8
800 cps	744.5	497.7	246.8
1 kc	744.5	497.7	246.8
3 kc	744.6	497.7	246.9
6 kc	744.6	497.7	246.9
10 kc	744.6	497.7	246.9
15 kc	744.6	497.7	246.9
20 kc	744.5	497.6	246.9
30 kc	744.4	497.5	246.9
40 kc	744.4	497.5	246.9
50 kc	744.4	497.5	246.9
60 kc	744.4	497.5	246.9
80 kc	744.3	497.5	246.8
100 kc	744.3	497.4	246.9
120 kc	744.3	497.4	246.9
200 kc	744.0	497.3	246.7
300 kc	743.7	497.2	246.5
400 kc	743.4	497.1	246.3
420 kc	743.3	497.0	246.3
450 kc	743.2	496.9	246.3

The differential method had to be proven accurate for determination of molecular weight. To do this the substitution method, which is an established accurate method, was used as comparison. In Table XI is shown a differential method on the identical fraction and concentration as was shown in Table IX with the substitution method. In Table XII the dielectric dispersion results of the differential and substitution determinations are shown as well as the difference between the dielectric dispersion of the differential and substitution methods. This would seem to conclusively prove the validity of such a method. The above results are not the only such made but the above was the only one included to avoid repetition.

This then seems to be all the preliminary measurements that had to be made.

Measurement of Concentrated Polymer Solutions - 5.0 grams/100 ml. solution of cellulose acetate in dioxane resulted in a 2.0 - 4.0 micro microfarad drop over the dispersion region. A dilute solution, 0.5 grams/100 ml. resulted in such a small drop that doubt existed as to the dispersion. It was concluded that ethyl cellulose would behave in much the same manner since the only essential difference is the ether linkage rather than the ester linkage.

A solution of ethyl cellulose was prepared in the following way. Approximately 5.0 grams of ethyl cellulose was dried in an oven at 105.0°C for a period of one hour. The sample

TABLE XI

Differential Method　　　　　　Ethyl Cellulose in Dioxane
F-6　　0.3 grams/100 ml.

Frequency	Capacity (Cell In)	Capacity (Cell Out)	ΔC
400 cps	113.70	97.50	16.20
500 cps	113.68	97.50	16.18
600 cps	113.62	97.50	16.12
800 cps	113.58	97.50	16.08
1 kc	113.54	97.50	16.04
2 kc	113.48	97.50	15.98
3 kc	113.40	97.50	15.90
6 kc	112.98	97.50	15.48
8 kc	112.90	97.50	15.40
10 kc	112.84	97.50	15.34
15 kc	112.51	97.50	15.01
20 kc	112.19	97.40	14.79
30 kc	111.67	97.30	14.37
35 kc	111.46	97.30	14.16
40 kc	111.31	97.30	14.01
50 kc	110.98	97.30	13.68
60 kc	110.79	97.30	13.49
80 kc	110.40	97.30	13.10
100 kc	110.19	97.30	12.89
120 kc	110.00	97.30	12.70
200 kc	109.58	97.20	12.38
300 kc	109.30	97.10	12.20
340 kc	109.23	97.10	12.13
360 kc	109.20	97.10	12.10
400 kc	109.20	97.10	12.10

TABLE XII

Dielectric Dispersion of Differential & Substitution Methods

F-6 0.3 grams/100 ml.

Frequency	Dielectric Dispersion (Differential)	Dielectric Dispersion (Substitution)
400 cps	1.00	1.00
500 cps	1.00	1.00
600 cps	1.00	1.00
800 cps	1.00	1.00
1 kc	.973	.952
2 kc	.949	.929
3 kc	.929	.905
6 kc	.826	.881
8 kc	.807	.857
10 kc	.792	.833
15 kc	.711	.714
20 kc	.658	.690
30 kc	.555	.571
35 kc	.504 -- C 35.1 kc	.500 -- C 35.0 kc
40 kc	.489	.452
50 kc	.386	.381
60 kc	.340	.333
80 kc	.245	.190
100 kc	.193	.167
120 kc	.147	.095
200 kc	.093	.024
300 kc	.050	0
340 kc	.007	0
360 kc	0	0
400 kc	0	0

was then placed in a dessicator until cool and then weighed to the nearest 0.1 milligram. The sample was placed in a 500 cc. glass-stoppered flask and 100 cc. of dioxane was added. The flask was mechanically agitated at 70°C until dissolution was assured.

The solution was then placed in the capacitance cell making certain that no air bubbles were trapped between the electrodes. The temperature of all runs was maintained at 25.0°C by a constant temperature room. Humidity was controlled at 50%.

The cell filled with solution was then placed in the substitution side of the bridge and the cell filled with solvent in the direct side. Measurements were then made over the entire frequency range and the hot leads of the cells were disconnected and the entire frequency range was again covered. With the differential method this is necessary in order to take into account the possible change in the instruments over the range.

From both sets of values, a subtraction was made and a ΔC was obtained. The results of this run are shown in Table XIII.

It is obvious from the above results that either a serious error was made or an enormous drop was encountered. The possibility of error was double checked and results were reproduced on three separate solutions. This drop was so large that it served no real purpose. The cell that contained such

TABLE XIII

Differential Method   Ethyl Cellulose in Dioxane
F-6   5.0 grams/100 ml.   Original material

Frequency	Cell In	Cell Out	ΔC
400 cps	705.0	397.9	307.1
500 cps	702.1	397.9	304.2
600 cps	700.5	397.9	302.6
800 cps	696.9	397.9	299.0
1 kc	694.5	397.9	296.6
2 kc	688.1	397.9	290.2
3 kc	684.7	397.9	286.8
6 kc	679.5	397.9	281.6
10 kc	676.3	397.9	278.4
15 kc	674.0	397.9	276.1
20 kc	672.2	397.9	274.3
30 kc	670.7	397.8	272.9
40 kc	669.5	397.8	271.7
50 kc	669.1	397.8	271.3
60 kc	668.9	397.7	271.2
80 kc	668.7	397.7	271.0
100 kc	668.5	397.7	270.8
120 kc	668.3	397.6	270.7
200 kc	665.0	397.4	267.6
300 kc	660.2	397.2	263.0
340 kc	652.3	397.1	255.2
400 kc	650.0	397.0	253.0

a viscous solution was difficult to clean and even though material was recovered, some was lost. For the above reason dilute solutions could be used that would give a satisfactory drop over the frequency range.

Dilute Solution Measurements - It is advantageous to be able to work with dilute solutions due to the fact that the solution laws hold to a greater extent in this region. Entanglement is held to a minimum in this region and extrapolation to zero concentration is much more certain.

For the numerous reasons above a 0.5 grams/100 ml. solution was prepared as previously described and measurements were made on ethyl cellulose in different solvents and different concentrations.

Due to the fact that ethyl cellulose is soluble in such a wide variety of solvents, it proves of interest to be able to observe the effect of solvents on fractions. Dioxane was the first chosen for investigation.

The sample was prepared, as before described, and from preliminary work it was decided to use solutions of concentrations 0.5, 0.4, 0.3, 0.2 grams/100 ml. Each of these gave a sufficient drop to yield reliable results. In fact, the drops obtained from the above concentrations were greater than or equal to the drop of cellulose acetate in dioxane using a concentration of 5.0 grams/100 ml.

Determinations concerning these samples yielded a most interesting phenomena before any results were obtained. It was suspected that critical frequencies obtained when plotted versus molecular weight would lie in a straight line. This, however, did not prove to be the case. Results were quite irregular and no definite conclusions were drawn. It was suggested that samples might not be completely in solution and some degree of association could exist. With this possibility in mind a rotator was constructed in an oven, and the oven was set 5-10 degrees below the boiling point of the solvent. Each sample solution was rotated in this oven before using and it was determined that 6-10 hours were needed before reproducible results could be obtained. The variation in the time of treatment was due to the concentration of solution. It was decided that all samples would be treated overnight.

Other difficulties were encountered with dioxane-ethyl cellulose systems. The solution could not be allowed to remain in the cell for a period exceeding four hours as a considerable amount of water was absorbed. This led to an increase in conductivity which in turn led to difficulties discussed later.

Difficulties were encountered at first in obtaining a proper leveling portion, C_∞ , at the higher frequencies. This was satisfactorily solved by using a substitution method with a parallel resonance filter (previously described) placed across the leads to the null detector.

Difficulty was also encountered in obtaining a C_o , the level portion at low frequencies. To eliminate this difficulty the fractions of McNeer (79) were refractionated as before described. This led to the obtaining of a level portion of the curves at high frequencies. Below is Table XIV covering the frequency range, showing a level portion at both high and low frequencies, as well as the calculation of the critical frequency as is described later.

As soon as all difficulties had been explained and remedied measurements on all sharp fractions were made to determine the critical frequency. The critical frequency is obtained from the dielectric dispersion, $D = \frac{\Delta c - \Delta c_\infty}{\Delta c_0 - \Delta c_\infty}$, in the following manner. The Δc_∞ is substracted from all values of Δc. This results in a series of values of $\Delta c - \Delta c_\infty$. The difference in $\Delta c_0 - \Delta c_\infty$ is found and the reciprocal of this value is multiplied throughout the frequency range by the value of $\Delta c - \Delta c_\infty$. By an appropriate plot of dispersion versus log frequency plus one, Figure 17, the critical frequency is determined as the point at which the dispersion is 50% complete.

After critical frequencies (ν_c) for all fractions had been calculated for all concentrations ranging from 0.2 grams/100 ml. to 0.5 grams/100 ml. they were plotted versus concentration. In Figure 18 are shown the results of such a plot. Examination of this graph shows that the critical frequencies are independent of concentration. This would indicate that only duplicate measurements need be taken at a single concentration. This would allow one to determine the (ν_c) of a sample in a minimum of ten

TABLE XIV

Differential Procedure Ethyl cellulose in Dioxane

Fraction 8 0.2 grams/100 ml.

Frequency (kc.)	ΔC		$(\Delta C_0 - \Delta C_\infty)$	Dispersion
0.4	8.73	ΔC_0	2.72	1.00
0.5	8.72		2.72	1.00
0.6	8.71		2.72	1.00
0.8	8.74		2.72	1.00
1.0	8.71		2.72	1.00
2.0	8.69		2.69	0.99
3.0	8.66		2.66	0.98
4.0	8.61		2.61	0.96
10.0	8.36		2.36	0.87
20	7.96		1.96	0.72
30	7.64		1.64	0.60
40	7.41		1.41	0.52
50	7.21		1.21	0.44
60	7.05		1.05	0.38
80	6.80		0.80	0.29
100	6.61		0.61	0.22
200	6.20		0.20	0.07
250	6.00	ΔC_∞	0	0
280	6.00		0	0
300	6.00		0	0
400	6.00		0	0

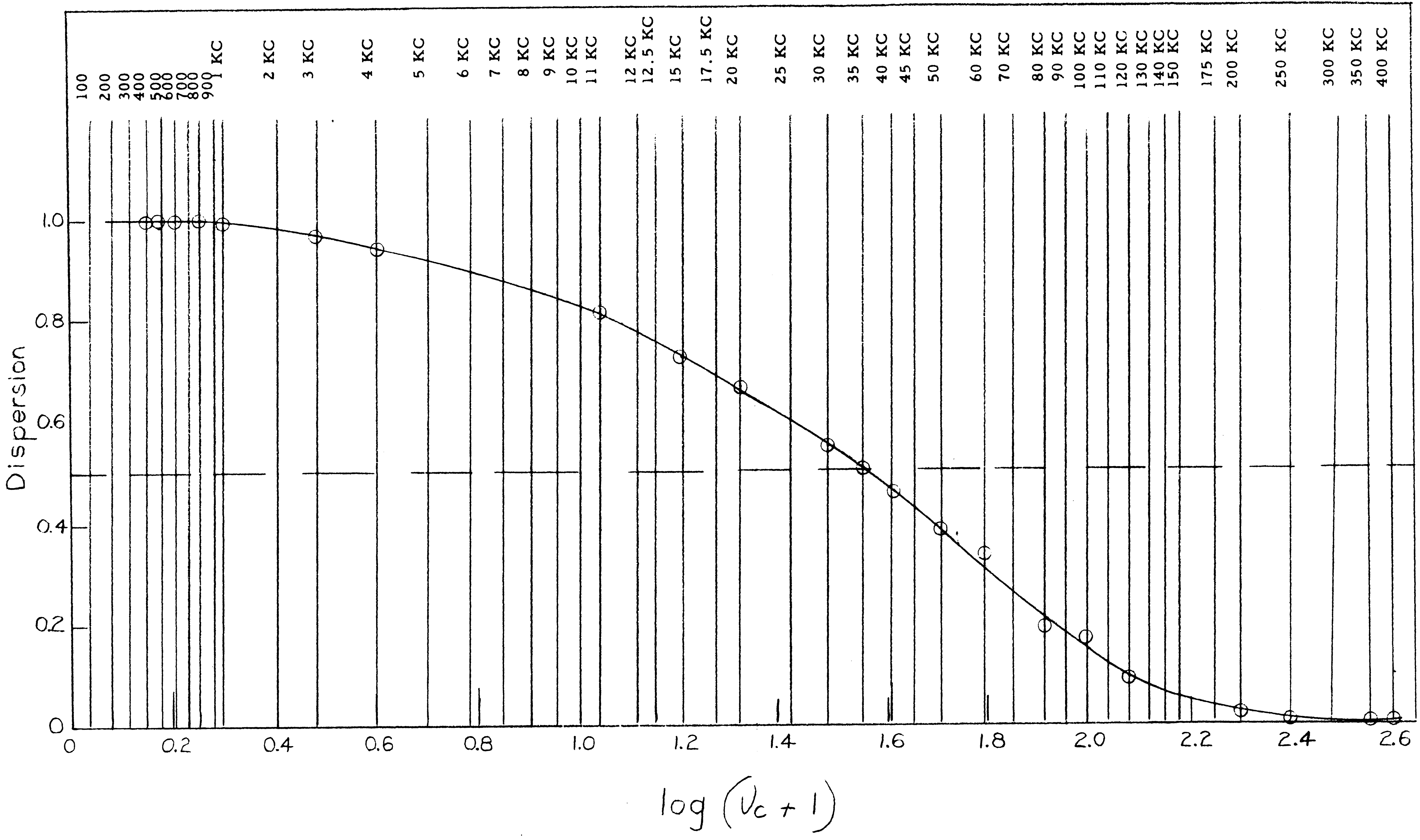
$$\begin{aligned} \Delta C_0 &= 8.72 \\ \Delta C_\infty &= \underline{6.00} \\ \Delta C &= 2.72 \end{aligned}$$

Dispersion = 1/2.72 (ΔC - 6.00)

Critical Frequency = 41.6 kc

FIGURE 17

Method of Determining the Critical Frequency



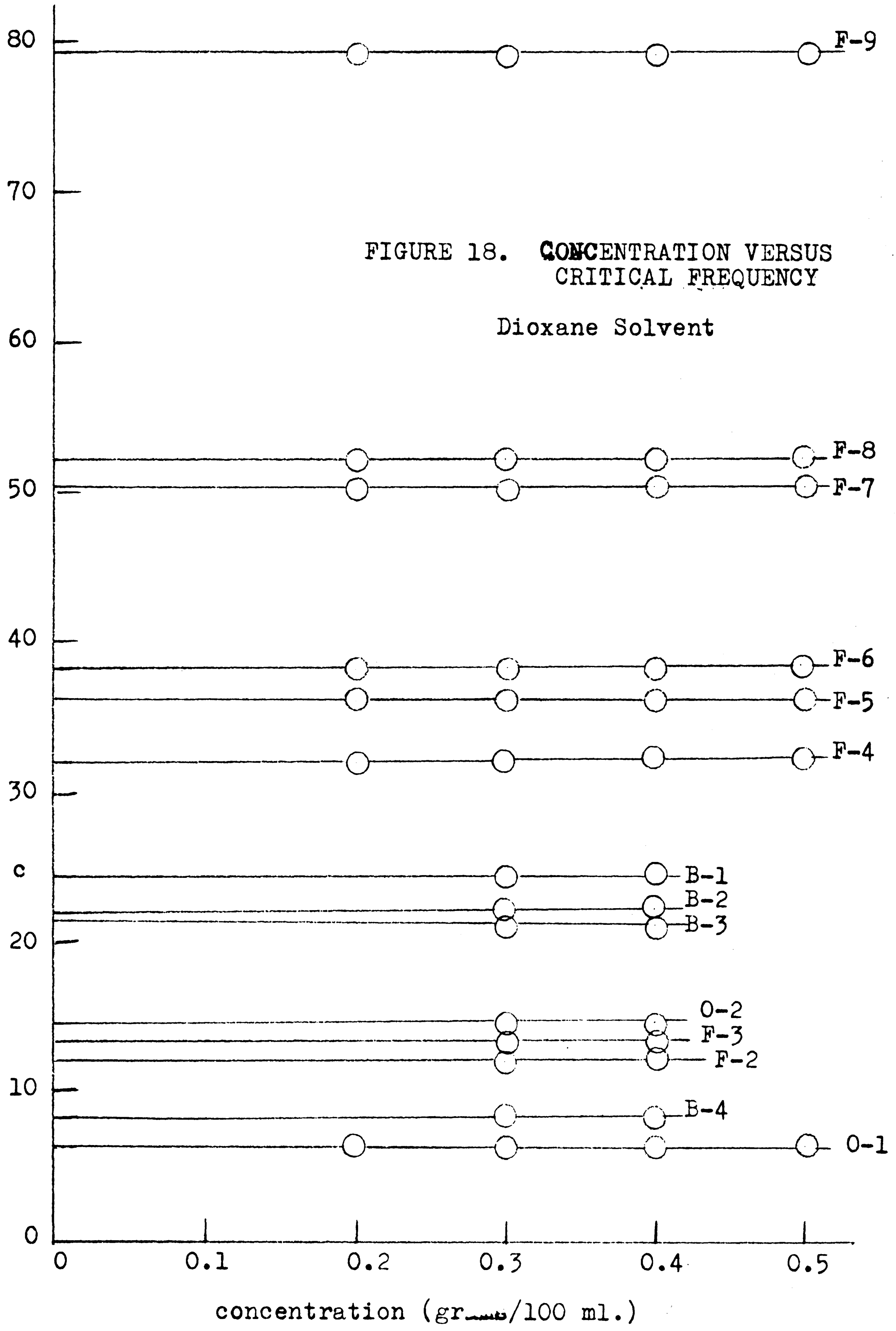


FIGURE 18. CONCENTRATION VERSUS CRITICAL FREQUENCY

Dioxane Solvent

minutes. Also shown in Table XV are the critical frequencies extrapolated to infinite dilution and results of viscosity determinations. In Figure 19 is plotted the log of the critical frequency (ν_c) versus log of the intrinsic viscosity. The equation of the straight line obtained from the above plot is

$$\log (100 [\eta]) = 2.97 - 0.59 \log (\nu_c)$$

As a check, critical frequencies (ν_c) of originals and blends were determined as unknowns. The intrinsic viscosities were determined by independent operators after the (ν_c) had been determined.

The investigator feels that the molecular weight can quickly and easily be determined for ethyl cellulose in dioxane as previous results (97) show the same to be true with cellulose acetate in dioxane. It should also be of interest to determine if the above is true with other solvents. Of equal importance is the effect of other solvents on the critical frequencies. For this reason further investigations were made in benzene, toluene, carbon tetrachloride, and n-butyl acetate.

Benzene solutions of ethyl cellulose were prepared in the same manner as was described for ethyl cellulose in dioxane. Critical frequencies were also determined in the same manner as previously shown.

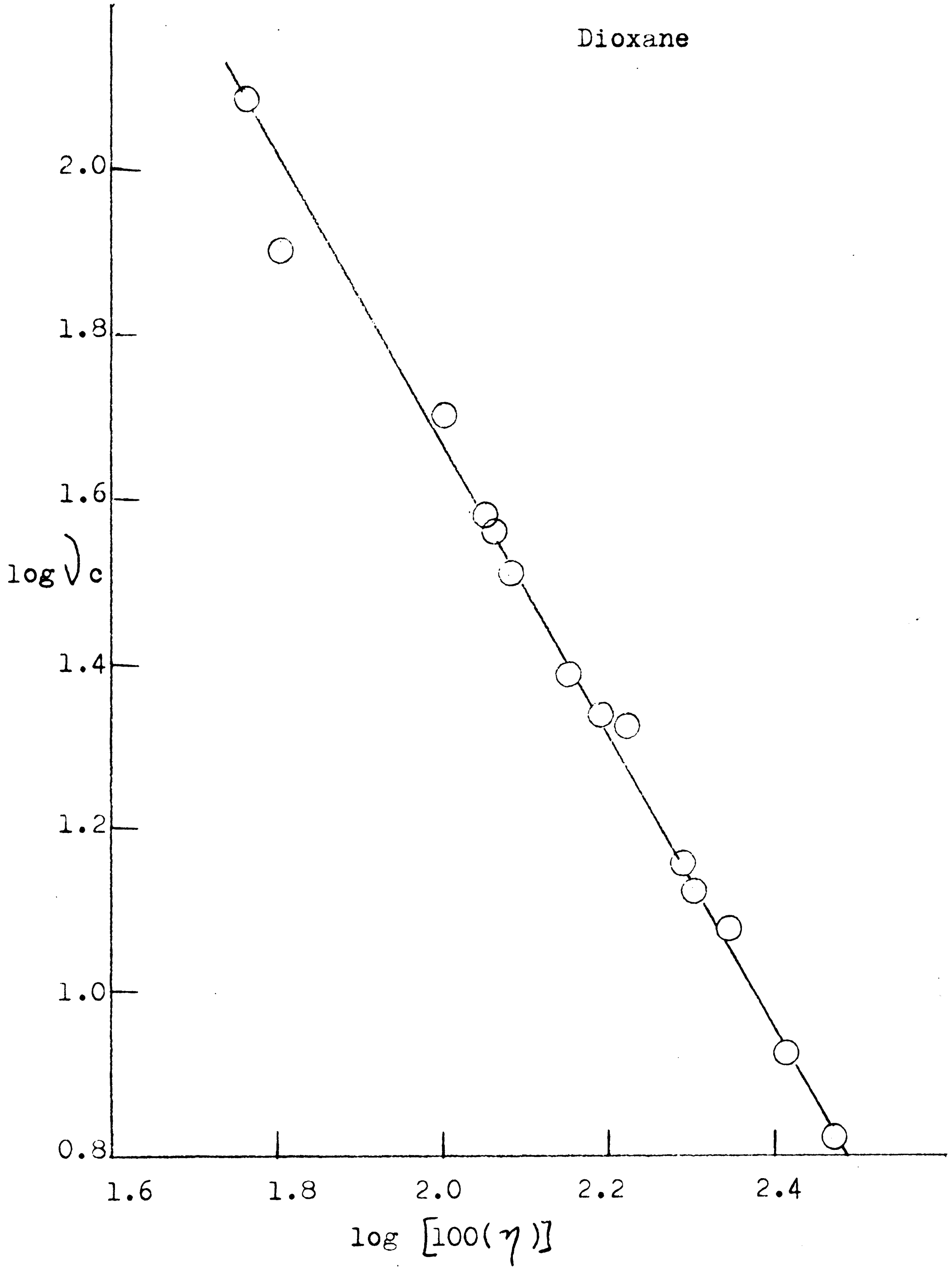
TABLE XV

Experimental Data for Ethyl cellulose in Dioxane

Sample	% Ethoxy	$[\eta]$ (dl/g) 25°	Critical Frequency (KC)	Huggins Constant k'
F - 1	48.7	3.01	6.5	0.37
F - 2	47.6	2.20	12.0	0.57
F - 3	47.6	1.98	13.4	0.66
F - 4	48.7	1.18	32.2	0.79
F - 5	48.7	1.15	36.2	0.67
F - 6	48.7	1.12	38.2	0.85
F - 7	48.7	1.00	50.5	0.44
F - 8	48.7	0.92	52.2	0.69
F - 9	48.7	0.63	79.5	—
O - 1	49.2	2.98	6.6	0.45
O - 2	47.6	1.93	14.5	0.50
B - 1	48.7	1.41	24.3	0.36
B - 2	48.7	1.54	22.1	0.49
B - 3	48.7	1.65	21.5	0.41
B - 4	48.7	2.59	8.6	0.49

Note: O - 1 and O - 2 are original unfractionated materials
B - 1, 2, 3, 4 are artificially prepared blends from fractions.

FIGURE 19. CRITICAL FREQUENCY VERSUS INTRINSIC VISCOSITY



Difficulty arose in the case of benzene solutions in obtaining a ΔC_o . Instead of the usual level portion the capacity differencies approached the zero axis asymptotically. In order to solve the problem a method used by Johnson and Cole (60) was employed. They used a corrective equation for a type of polarization that took the form :

$$\epsilon_{\text{real}} = \epsilon_{\text{measured}} + k/\omega^2$$

By a substitution of ΔC in place of ϵ , a straight line was obtained when 10^2 over omega squared was plotted versus the ΔC . An example of such a plot is shown in Figure 20. From the plot the real value of ΔC_o could be found, and using this value no trouble was found in obtaining critical frequencies.

In the case of ethyl cellulose in benzene an oven treatment was necessary since irregularities again appeared if the solution was not oven treated.

Quite an interesting result is noted when the (ν_c) is plotted versus the concentration (Figure 21). The critical frequencies show a very definite concentration dependence. A possible explanation of such phenomena will be offered in a later section.

As was true with ethyl cellulose in dioxane, the log of (ν_c) was plotted versus log (100 $[\eta]$), and a straight

FIGURE 20. DETERMINATION OF ΔC_0 BY JOHNSON COLE RELATIONSHIP

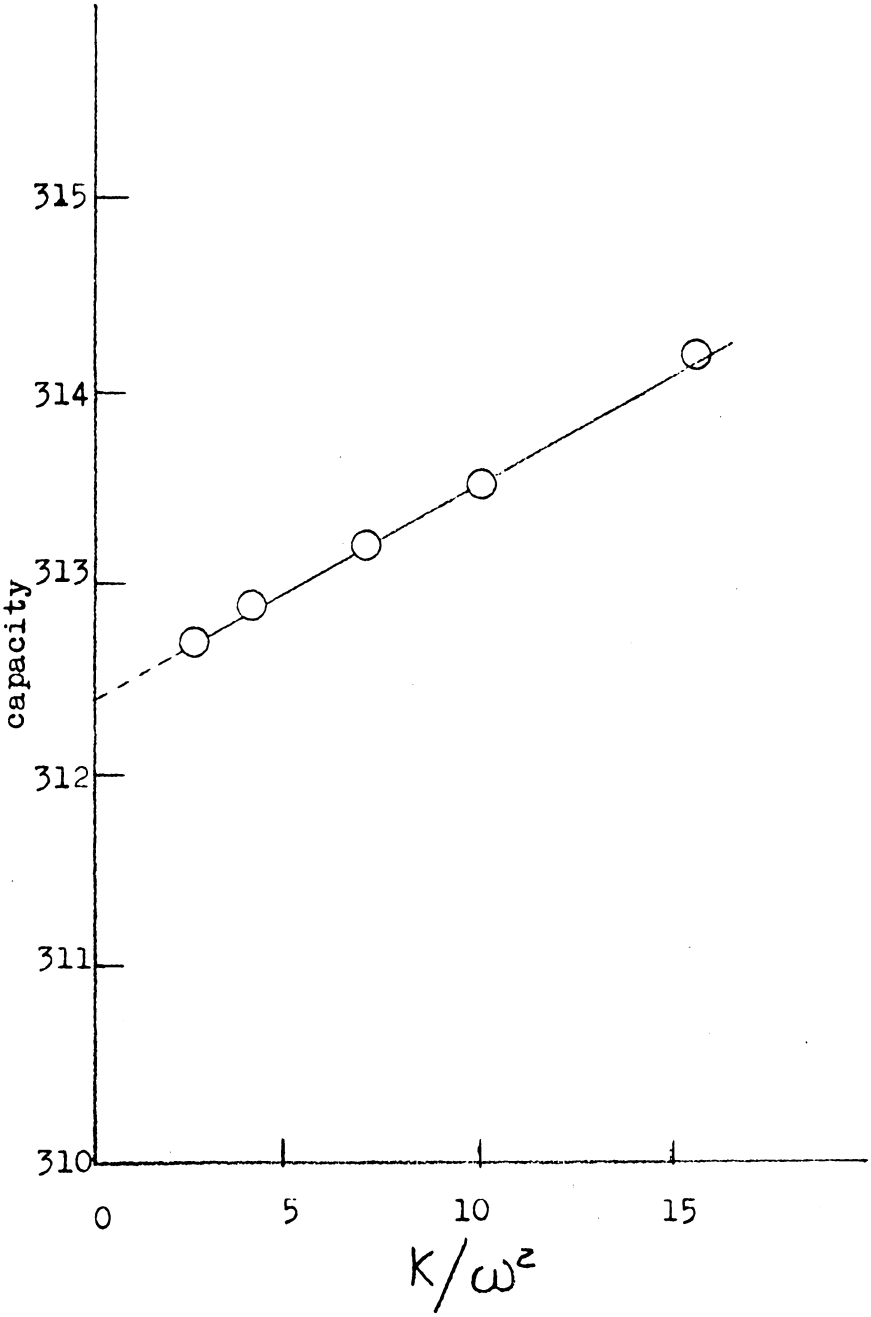
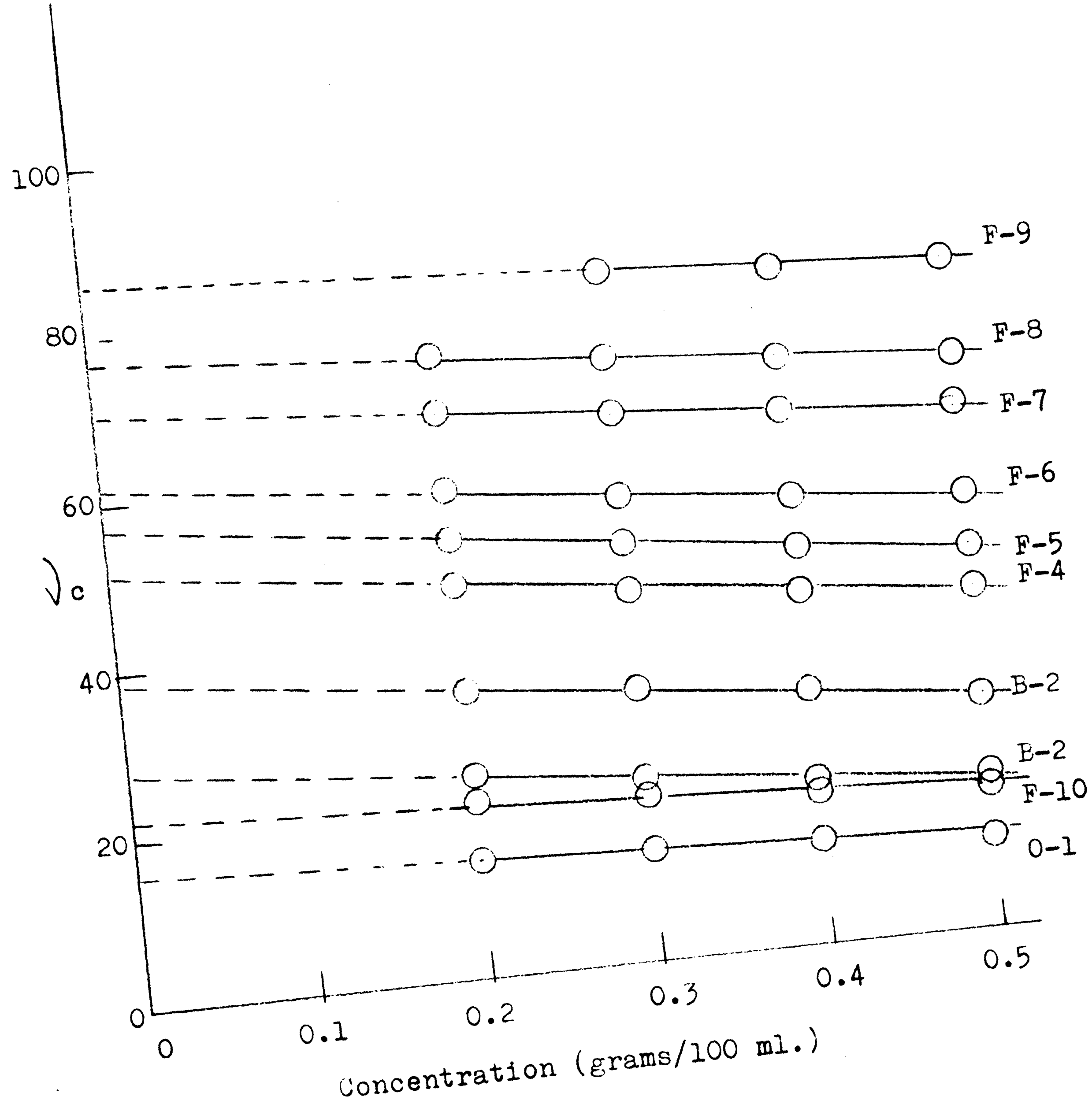


FIGURE 21. CONCENTRATION VERSUS CRITICAL FREQUENCY

Benzene Solvent



line resulted (Figure 22) from which an equation could be fitted.

$$\log (100[\eta]) = 3.41 - 0.82 \log (\nu_c)$$

Toluene solutions of ethyl cellulose were prepared as above described and critical frequencies were thus determined in exactly the same manner.

It was likewise proven in the case of toluene that an oven treatment was necessary by measuring a fraction of ethyl cellulose in toluene. In one case the solution was not oven treated before measuring and in the other case the same fraction was subjected to the overnight treatment and then measured. For regularity of results the treatment was necessary.

It was not surprising that in the case of toluene solutions that a slight polarization would occur as was true in benzene. The two solvents are quite similar and would be expected to behave in like manner. The extrapolation to zero frequency was necessary as was shown above in Figure 20.

Ethyl cellulose in toluene behaved in a manner quite similar to benzene also in regard to the concentration dependence. Figure 23 shows the concentration versus the critical frequency for the fractions investigated. Not as many fractions were investigated since the aim was to show the comparison with benzene as a solvent and to determine the correlation between the molecular weight and the critical frequency.

FIGURE 22. CRITICAL FREQUENCY VERSUS INTRINSIC VISCOSITY

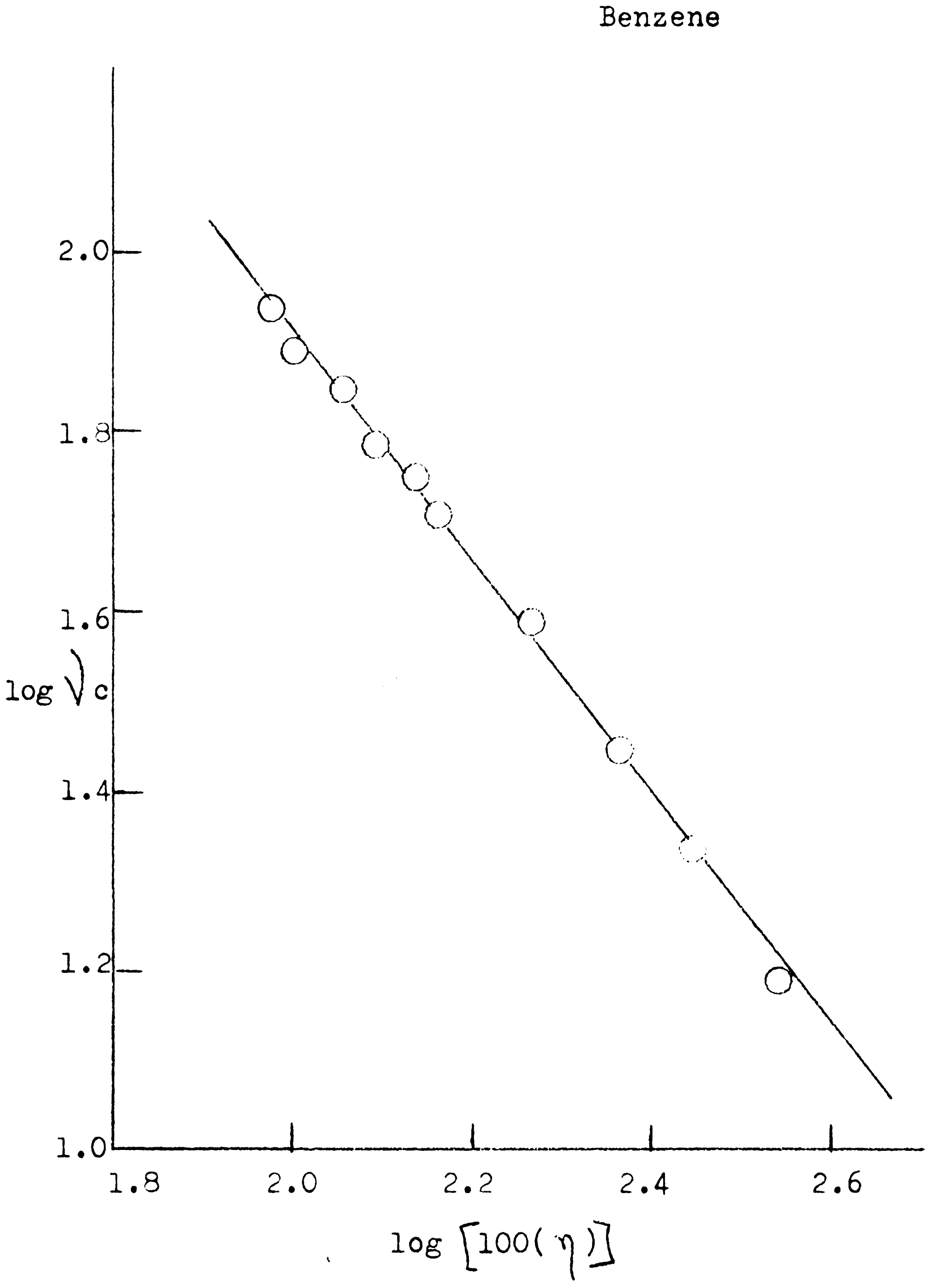
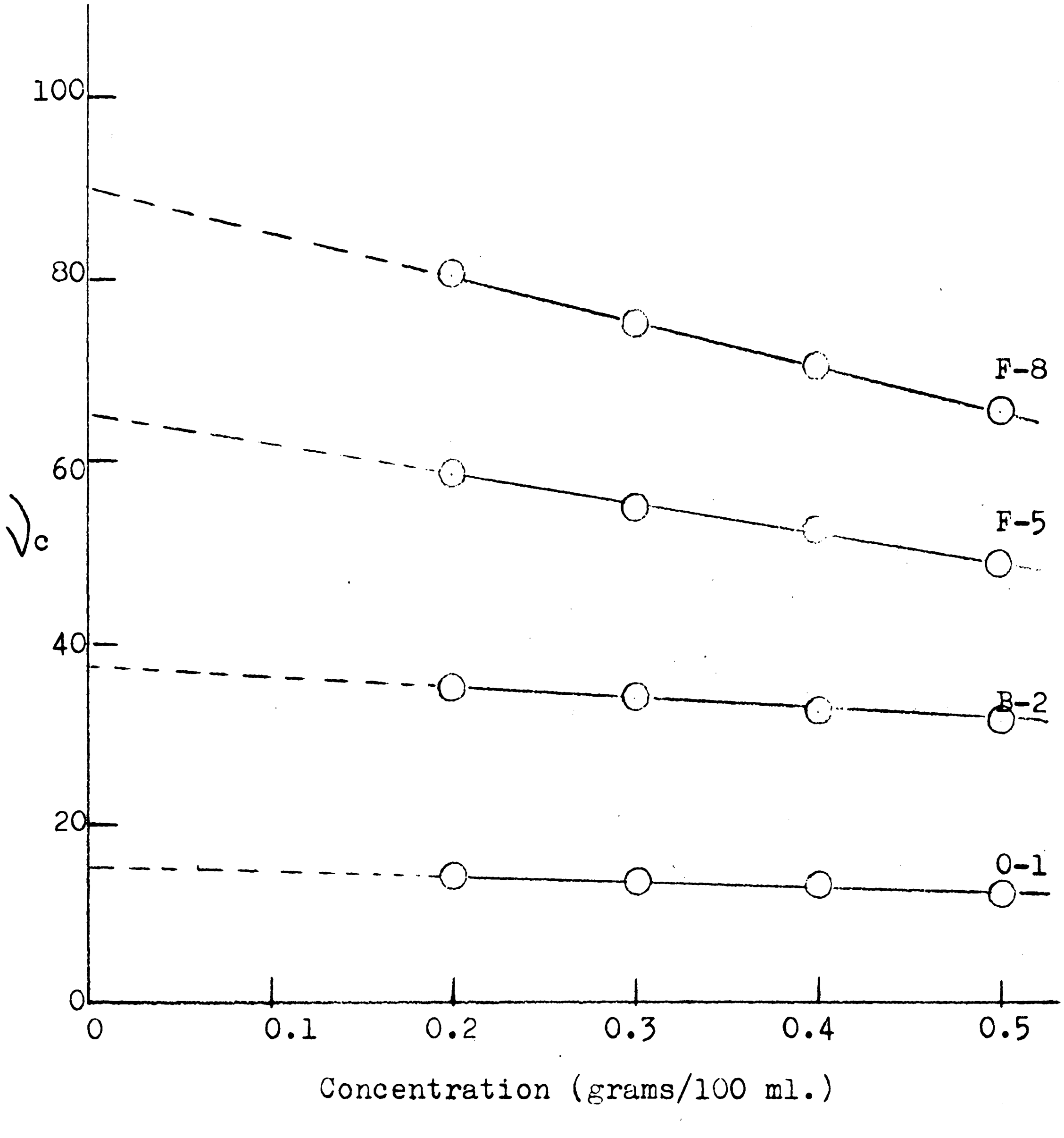


FIGURE 23. CONCENTRATION VERSUS CRITICAL FREQUENCY

Toluene Solvent



From the equation below and the plot of log $(100[\eta])$ versus log (ν_c) (Figure 24), it is obvious the same relation held for ethyl cellulose in toluene as was true with ethyl cellulose in benzene and dioxane.

$$\log (100[\eta]) = 3.23 - 0.65 \log (\nu_c)$$

Carbontetrachloride solutions of ethyl cellulose showed the same slight polarization and necessitated the extrapolation to zero frequency to obtain ΔC_0. No trouble was encountered in this solvent, benzene, and toluene with respect to the C_∞.

Again an oven treatment was necessary as proven by experimental determination.

In the case of ethyl cellulose in carbontetrachloride the plot of concentration versus the critical frequency exhibited a concentration independence. This is shown in Figure 25.

Also from Figure 26 and the equation below the molecular weight relationship is valid.

$$\log (100[\eta]) = 3.41 - 0.83 \log (\nu_c)$$

Figures 27 and 28 shows the results of the (ν_c) for ethyl cellulose in the four solvents versus the log $(100[\eta])$ and log D. P. In Table XVI all of the above data is collected,

FIGURE 24. CRITICAL FREQUENCY VERSUS INTRINSIC VISCOSITY

Toluene

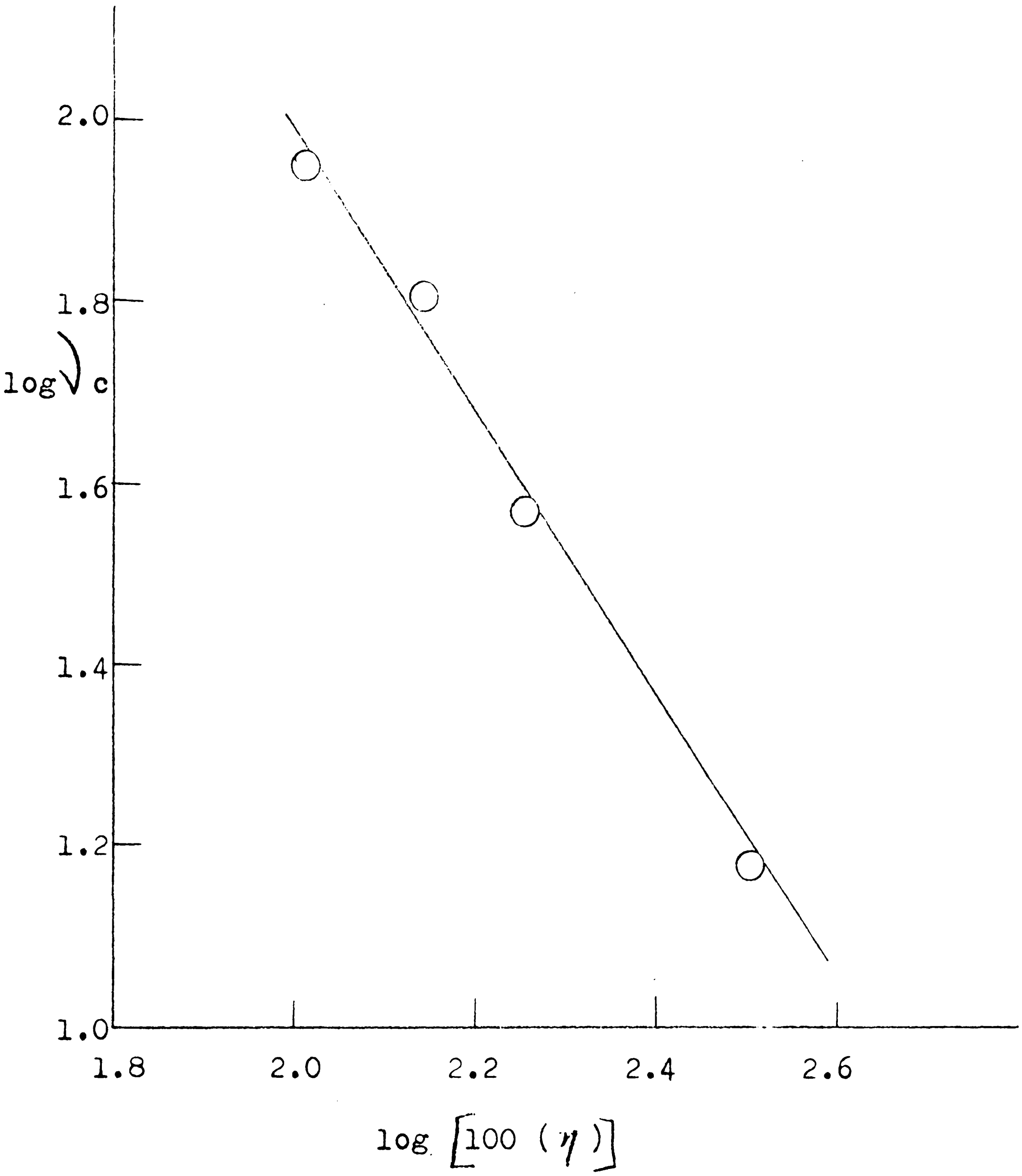


FIGURE 25. CONCENTRATION VERSUS CRITICAL FREQUENCY

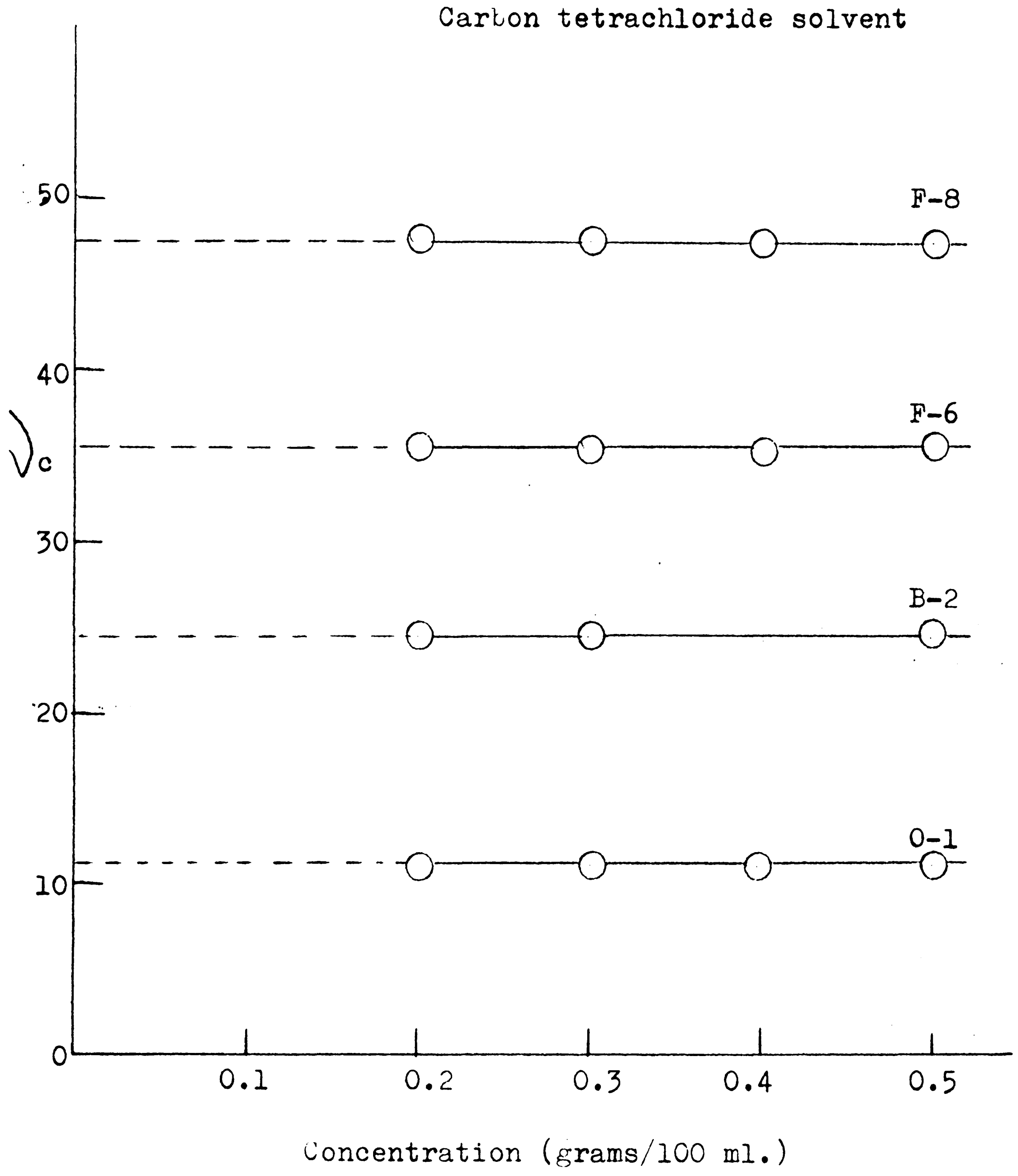


FIGURE 26. CRITICAL FREQUENCY VERSUS INTRINSIC VISCOSITY

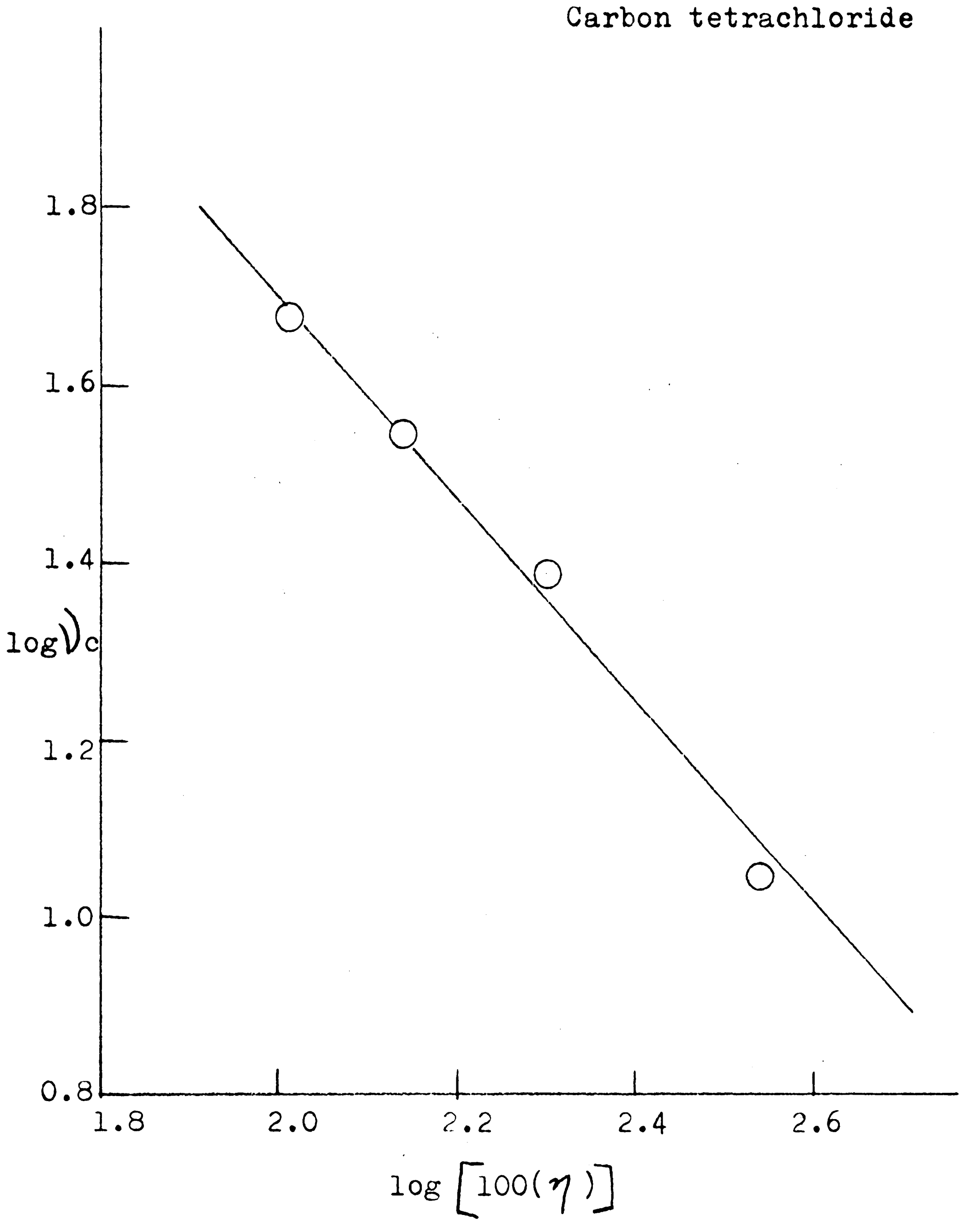


FIGURE 27. LOG INTRINSIC VISCOSITY VERSUS LOG CRITICAL FREQUENCY

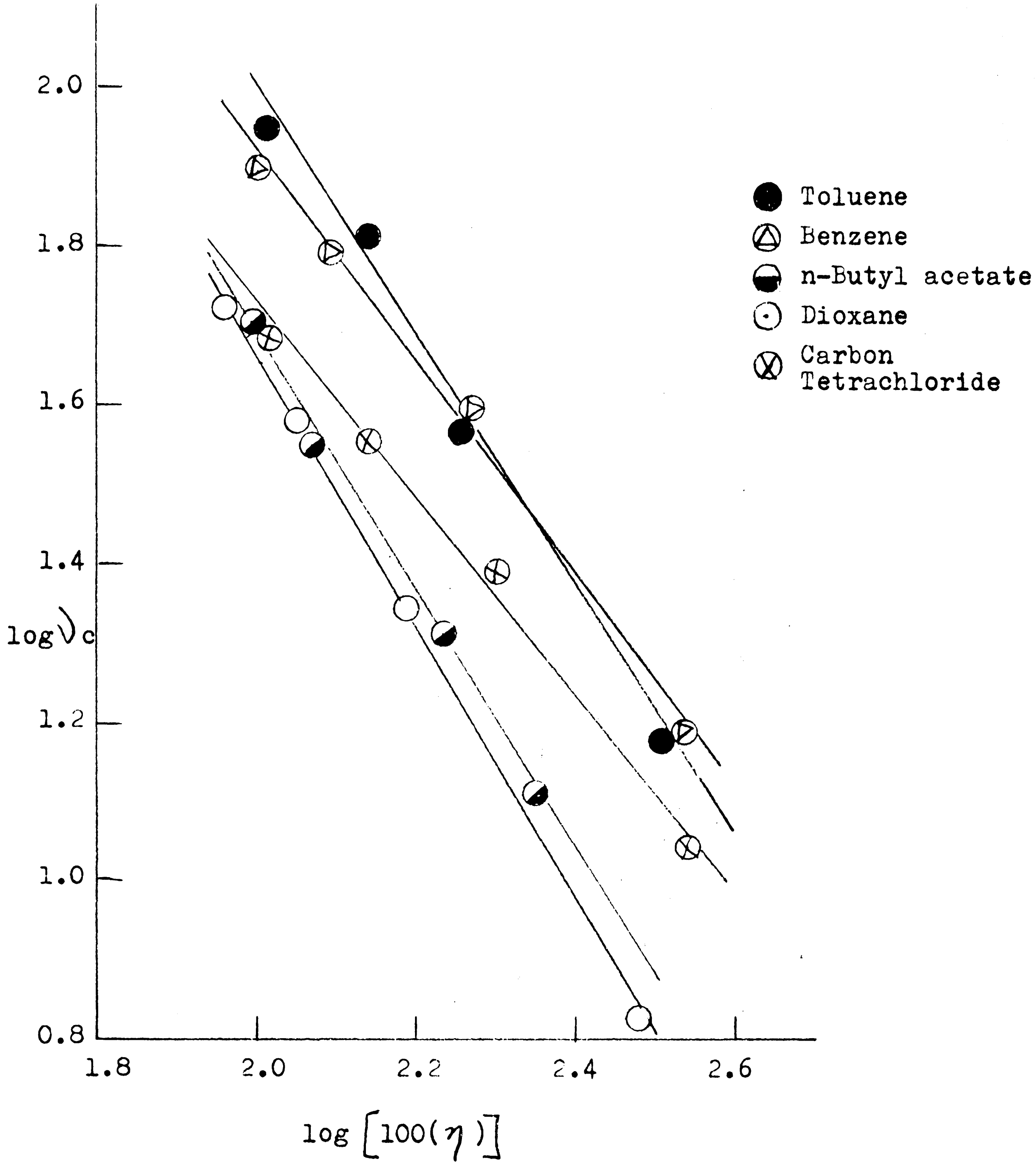


FIGURE 28. LOG D. P. VERSUS LOG ν_c

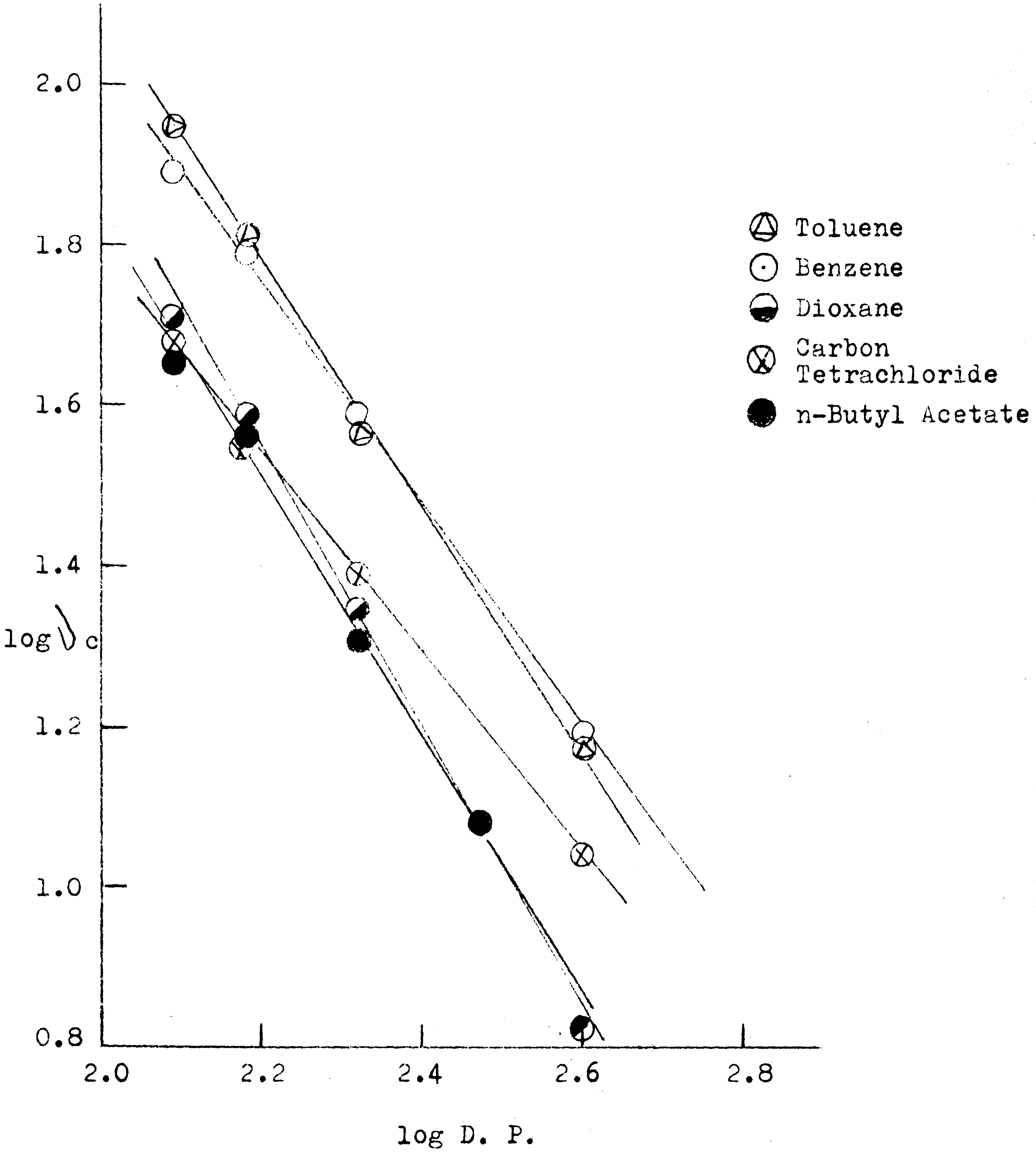


TABLE XVI

EXPERIMENTAL DATA FOR ETHYL CELLULOSE IN SOLUTION

	%		Dioxane		Carbon Tetrachloride			
Sample	Ethoxy	$[\eta]$	k'	$[\nu_c]$	$[\eta]$	k'	$[\nu_c]$	DP[b]
F-1	48.7	3.01	0.37	6.5				406
F-2	47.6	2.20	0.57	12.0				297
F-3	47.6	1.98	0.66	13.4				267
F-4	48.7	1.18	0.79	32.2				159
F-5	48.7	1.15	0.67	36.2				155
F-6	48.7	1.12	0.85	38.2	1.37	0.80	35.5	151
F-7	48.7	1.00	0.44	50.5				135
F-8	48.7	0.92	0.69	52.2	1.03	0.94	47.4	124
F-9	48.7	0.63		79.5				85
O-1	49.2	2.98	0.45	6.6	3.49	0.84	11.0	402
O-2	47.6	1.93	0.50	14.5				260
B-1	48.7	1.41	0.36	24.3				190
B-2	48.7	1.54	0.49	22.1	2.01	0.95	24.5	208
B-3	48.7	1.65	0.41	21.5				223
B-4	47.6	2.59	0.49	8.6				350

$[\eta]$ = Intrinsic Viscosity at 25°C (dl/g)

k' = Huggins Constant

$[\nu_c]$ = Critical Frequency (Kc) extrapolated to zero concentration

[b] Calculated using Hercules constant

(Continued)

TABLE XVI (Continued)

	Benzene			Toluene			n-Butyl Acetate			
Sample	$[\eta]$	k'	$[\nu_c]$	$[\eta]$	k'	$[\nu_c]$	$[\eta]$	k'	$[\nu_c]$	DP^b
F-1										406
F-2							3.00	0.60	12.8	297
F-3										267
F-4										159
F-5				1.37	0.90	64.8				155
F-6	1.22	0.68	62.0				1.25	0.83	35.2	151
F-7										135
F-8	0.99	0.72	77.1	1.02	0.59	90.0	0.98	0.70	44.7	124
F-9										85
O-1	3.47	0.63	15.5	3.18	1.01	15.2				402
O-2										260
B-1										190
B-2	1.84	1.08	39.0	1.77	1.27	37.3	1.75	1.10	20.5	208
B-3										223
B-4										350

$[\eta]$ = Intrinsic Viscosity at 25°C (dl/g)

k' = Huggins Constant

$[\nu_c]$ = Critical Frequency (Kc) extrapolated to zero concentration

^{b}Calculated using Hercules constant

including intrinsic viscosities, critical frequencies, ethoxy content, Huggins constants, and the degree of polymerization calculated from the Hercules Constant (91).

Attempts to Measure Ethyl Cellulose Dielectric Dispersion in Polar Solvents - The characteristics of polar solvents are quite different from those previously discussed. Dioxane, benzene and such all possess dielectric constants from 2.0 - 2.3. They are classed as non polar solvents. Polar solvents are solvents that have dielectric constants higher than the non polar solvents and in many cases possess a relatively high conductivity. This conductivity leads to a low resistance since it is the reciprocal of the conductivity. A high parallel resistance is necessary for measurement since the precision condenser or the bridge condenser possesses an infinite resistance. For a balance to be obtained the resistance and the capacity must be balanced. This may be seen from the simplified diagram below (Figure 29).

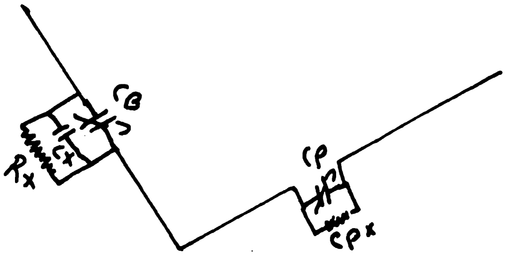


Figure 29

It is interesting to note that up to the present time no work can be found which employs high dielectric solvents at low frequencies. At higher frequencies the substitution and direct methods can be employed.

The fact was mentioned that a parallel resistance method might be applied. This method however leads to difficulties that have not been remedied to date. In the method the dissipation dial is set at zero and the decade resistor is adjusted for a resistance balance. This supplements the resistance of the solution which is lower than the resistance of the capacitor as described above. The balance is sharp and measurements can be made at any frequency. The regular substitution or direct method cannot be used since the dissipation is too large to allow measurement at low frequencies. With n-butyl acetate 10 Kc is the lowest frequency where the dissipation range is low enough to permit measurement.

Unfortunately, the decade resistance box possesses a capacitance that is included with that of the measuring condenser. To determine the actual change in capacity of the solution under investigation the capacitance of the resistance box must be subtracted. It cannot be assumed that the capacity of the box would remain constant with different dial reading and different frequencies. The bridge manual states the above is true and illustrates a method of evaluating the capacitance. This was attempted without success as the resistance setting was too low for measurements of capacitance. The resistance of the box must be appreciable at low frequencies for a direct measure of capacitance. At higher frequencies the resistance can be a great deal lower and measurements may be easily made. However, the parallel resistance method is not necessary at these higher frequencies.

Many attempts were made to measure the capacity of the decade resistance box. Condensers or resistors were placed in parallel with the bridge condenser by methods described in the General Radio Manual but all to no avail. The author has discussed this problem with numerous people, many well known authorities, and no suggestions were forthcoming for the measurement of the capacitance of the decade. It is noteworthy to mention that no application of this parallel resistance method can be found in the experimental literature concerning the above stated problem.

Gilkerson (41) constructed a special cell that made use of glass covered electrodes. A diagram of this cell is shown in Figure 30.

The use of this cell led to very sharp null points down to 100 cycles with acetone. The cell was used to measure cell constants by the use of liquids of known dielectric constants. An empirical equation was derived from the constants. The equation was derived on the basis of the following circuit of the cell.

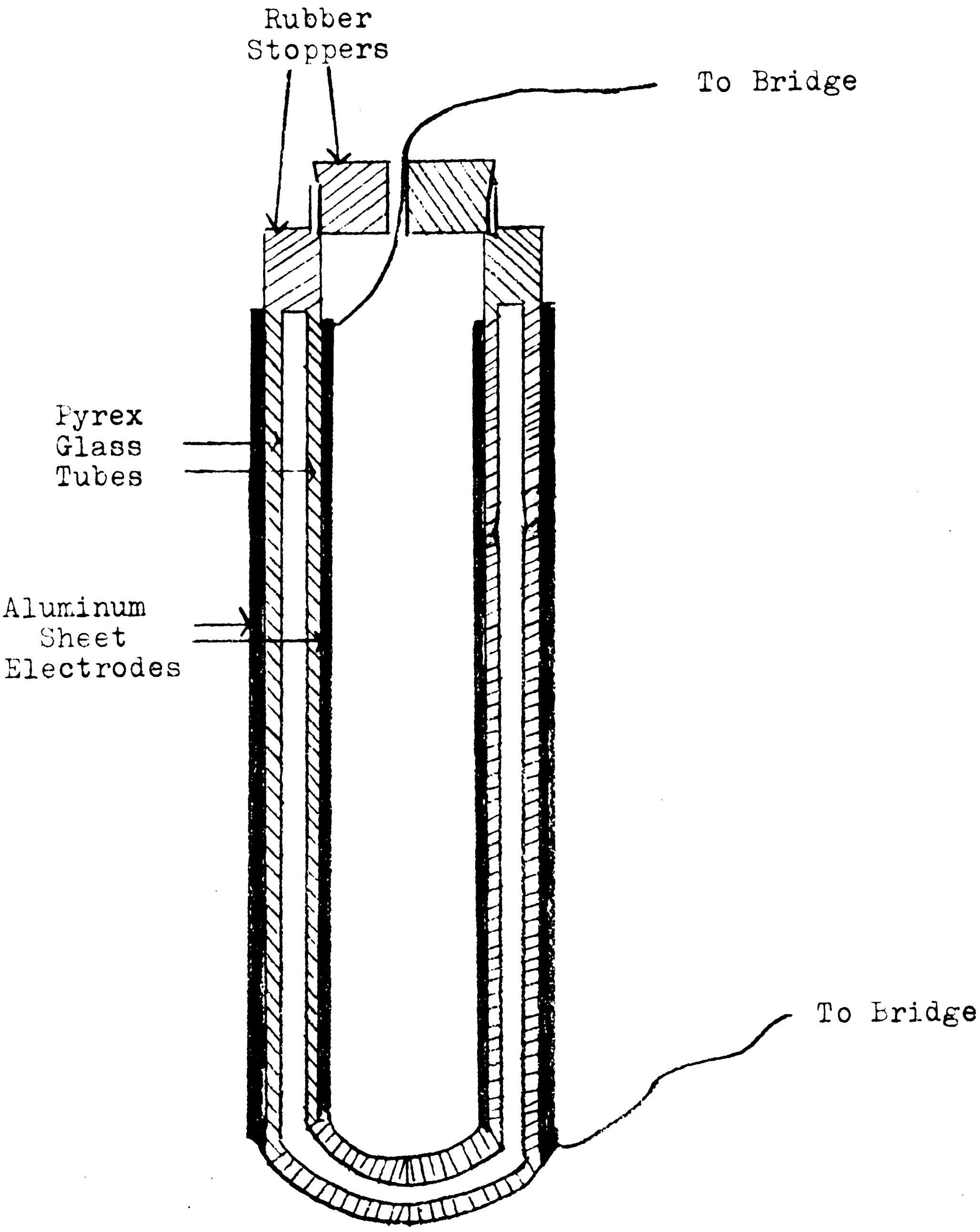
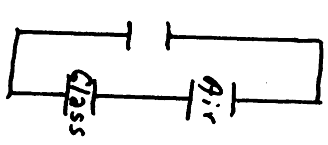
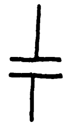


FIGURE 30. Cell with Glass Shielded Electrodes





Bridge Condenser

capacity of cell $\frac{1}{C_{cell}} = \frac{1}{Cg} + \frac{1}{Cx} = \frac{Cg + Cx}{CgCx}$

measured capacity with leads (Cd) = ϵ mx

$$Cmx = \frac{CgCx}{Cg + Cx} + Cd$$

Cg = capacity of glass

Cd = capacity of leads

$$Cmx = \frac{CgCs + CgCd + CdCx}{Cg + Cx}$$

Solving for C

$$Cx = \frac{Cg\ (Cd - Cmx)}{Cmx - (Cg + Cd)}$$

where Cme is capacity of cell measured empty

$$Ca = \frac{Cg\ (Cd - Cme)}{Cme - (Cg + Cd)}$$

$$\epsilon\, x = \frac{Cx}{Ca} = \frac{(Cd - Cmx)\ Cme - (Cg + Cd)}{Cmx - (Cg + Cd)\ (Cd - Cme)}$$

where ϵ x is the dielectric constant of the liquid.

By solving simultaneous equations the unknown values, such as the capacity of leads and combined capacity (Cd + Cg), could be found.

Using the above equation the dielectric constant of unknown liquids could be determined. Values for dioxane, benzene and n-butyl acetate are shown in Table XVII. It was hoped that instead of using the usual capacity change to measure the dielectric dispersion that it could be followed by observing the decrease in dielectric constant. Comparison with accepted values show that the dielectric constant in Table XVII is acceptable. There is slight polarization with n-butyl acetate but this can be corrected by the Johnson-Cole relationship already described.

$$\epsilon_{\text{true}} = \epsilon_{\text{measured}} + \frac{K}{\omega^2}$$

The method had to be discontinued for the present when solutions of ethyl cellulose in n-butyl acetate were measured. This appeared necessary since when the dielectric constants were calculated, the change with the frequency was very minute compared to a satisfactory decrease in the solution capacity needed for exact dispersion determination. This may be seen in Table XVIII. The drop would not allow accuracy in determination since much of the frequency range would possess the same dielectric constant. It was also found that for solvents of higher dielectric constant results were not in accord with values found in the literature. A possible explanation of such behavior will be given in Discussion of Results.

Temperature Effect - Attempts were made to shift the dispersion region by either increasing or decreasing the temperature. An increase in temperature should shift the

TABLE XVII

CALCULATED DIELECTRIC CONSTANTS OF LIQUIDS

25°C

Frequency (KC)	ϵ Benzene	ϵ Dioxane	ϵ But. Ac.
.4	2.316	2.385	18.228
.6	2.318	2.380	11.032
.8	2.304	2.373	8.793
1.0	2.306	2.374	7.789
3.0	2.289	2.364	5.940
6.0	2.284	2.365	5.342
8.0	2.284	2.352	5.684
10.0	2.285	2.360	5.685
20.0	2.279	2.346	5.609
30.0	2.272	2.347	5.590
40.0	2.274	2.341	5.592
50.0	2.282	2.350	5.612
60.0	2.282	2.343	5.612
80.0	2.272	2.343	5.574
100.0	2.272	2.343	5.556
120.0	2.272	2.343	5.556
140.0	2.272	2.336	5.537
160.0	2.281	2.345	5.557
180.0	2.281	2.345	5.539
200.0	2.273	2.345	5.539
240.0	2.282	2.346	5.559
280.0	2.282	2.346	5.541
300.0	2.282	2.346	5.541
360.0	2.275	2.340	5.541
400.0	2.275	2.340	5.522
Literature value	2.27	2.33	5.55

TABLE XVIII

DECREASE IN THE DIELECTRIC CONSTANT OF 1.0 grams/100 ml ETHYL CELLULOSE IN n-BUTYL ACETATE WITH FREQUENCY. GLASS CELL MEASUREMENT

Frequency	ϵ
400 cps	2.423
500 cps	2.423
600 cps	2.416
800 cps	2.381
1 Kc	2.373
3 Kc	2.367
6 Kc	2.352
10 Kc	2.345
20 Kc	2.330
30 Kc	2.331
40 Kc	2.330
60 Kc	2.304
80 Kc	2.289
100 Kc	2.293
120 Kc	2.293
200 Kc	2.293
300 Kc	2.293
400 Kc	2.293

entire dispersion region to higher frequencies. By doing this, it was hoped that measurement could be made starting with a higher frequency than usual. This would be advantageous in that polarization could be avoided. Unfortunately, even a marked increase in temperature, almost the boiling point of pure solvent, failed to bring about improvement. A slight shift was noted but not enough to markedly affect the dispersion region.

Many other methods have been tried. A condenser in series with the cell and resistor in series with the cell are two examples. In the majority of cases results were obtainable but no conclusions could be drawn or dispersion values calculated.

Network Method - A different approach was attempted in the hope of being able to measure the dielectric dispersion of ethyl cellulose in solvents of high dielectric constant. A resistance network was found (18) which could be adapted to the measurement of ethyl cellulose in n-butyl acetate. The network is shown in Figure 31 below:

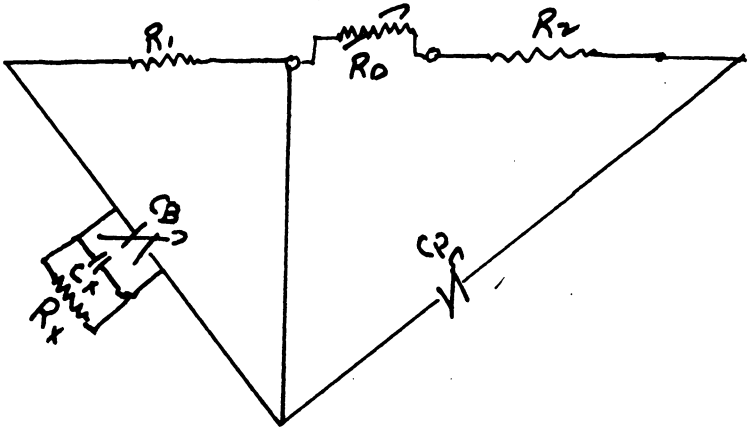


Figure 31

where C_p = precision condenser
C_B = bridge condenser
C_x = cell capacity
R_x = cell resistance
R_D = variable decade resistor
R_1 = fixed precision resistor - 1×10^6 ohms
R_2 = fixed precision resistor

By first measuring the resistance of the cell with the decade resistor the value of R_2 could be calculated and fixed in position. The value of such a resistor was selected so that for a resistance balance R_D must be approximately ten thousand ohms. R_1 was incorporated into the network so R_2 could be high and so reduce the capacity of the decade to a negligible quantity.

Polarization was again encountered and the same correction as was previously described was applied. Oven treatment was again a necessity. The solution if not treated showed a large variance in the critical frequency from the correct value. As the sample was treated for one hour the critical frequency approached the correct value. After eight hours the correct value was obtained with each previous hour's treatment further approaching the correct (ν_c).

The critical frequency of all fractions was determined in the same way as all previous solutions.

Again a concentration independence was noted as was found with dioxane and carbon tetrachloride solutions (Figure 32). The same correlation between the (ν_c) and the intrinsic viscosity was found as was also true with all previous work. The correlation is shown in Figure 33 and the equation for the curve is below.

$$\log (100[\eta]) = 3.23 - 0.85 \log (\nu_c)$$

The next step would seem to be the measurement of ethyl cellulose in solvents of even higher dielectric constants. The resistance of ethylene chloride, benzyl alcohol, n-butyl alcohol, and acetone as examples are quite a bit lower than that of butyl acetate. Since the resistance is lower, then the value of R_2 and R_D must be lower than with n-butyl acetate. If R_2 must be lower than what was used for n-butyl acetate, it would not cut down the capacity of the decade resistor R_D. Thus R_D would change with frequency. The criteria for such a network is that R_2 in series with R_D must be large. It should then be obvious that no other solvent can be used with the above mentioned network. The network unfortunately is only applicable with solvents of dielectric constants of 5.0 and below. The problem of measurement of high dielectric solvents still remained to be solved.

FIGURE 32. CONCENTRATION VERSUS CRITICAL FREQUENCY

n-Butyl Acetate

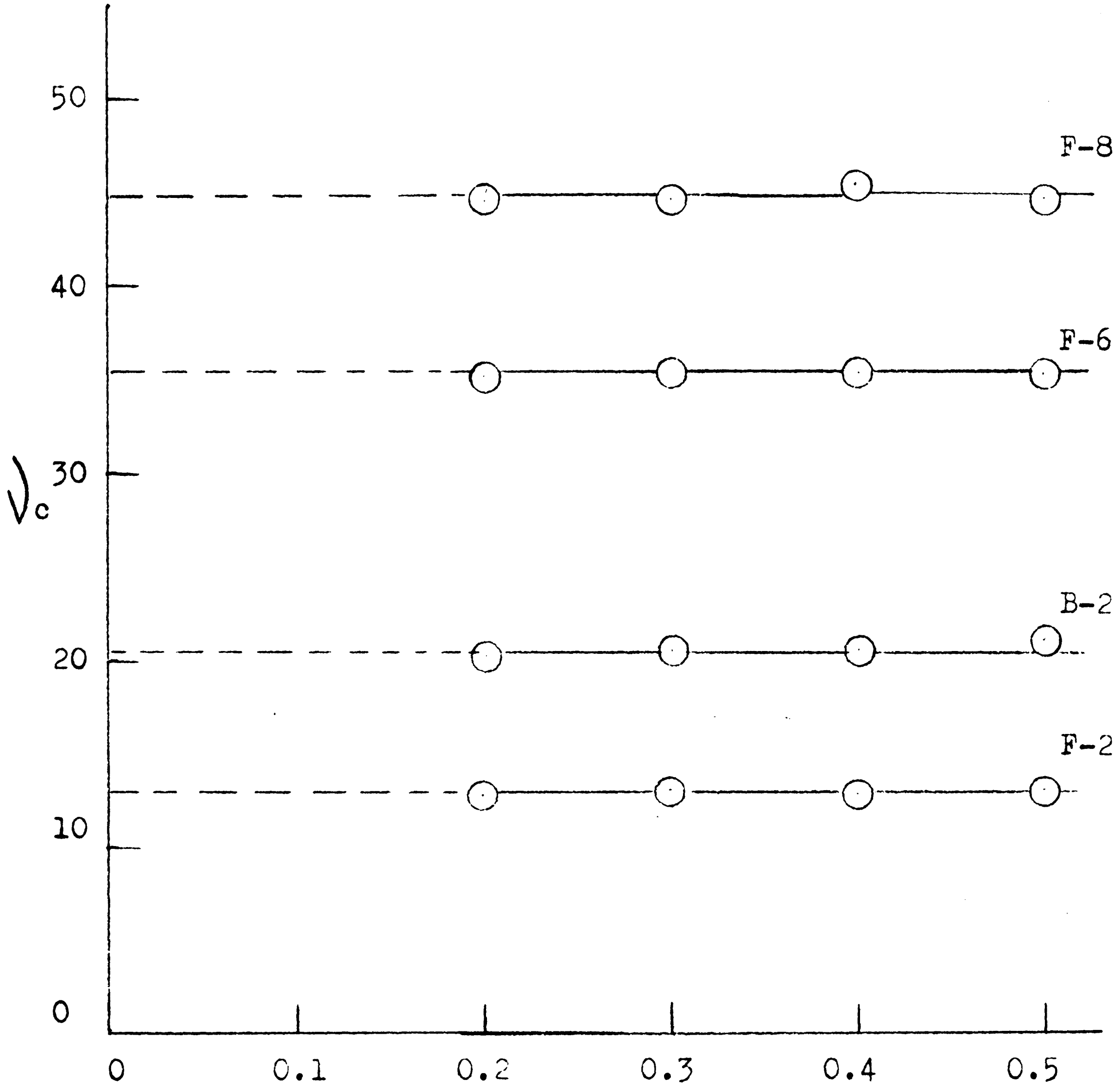
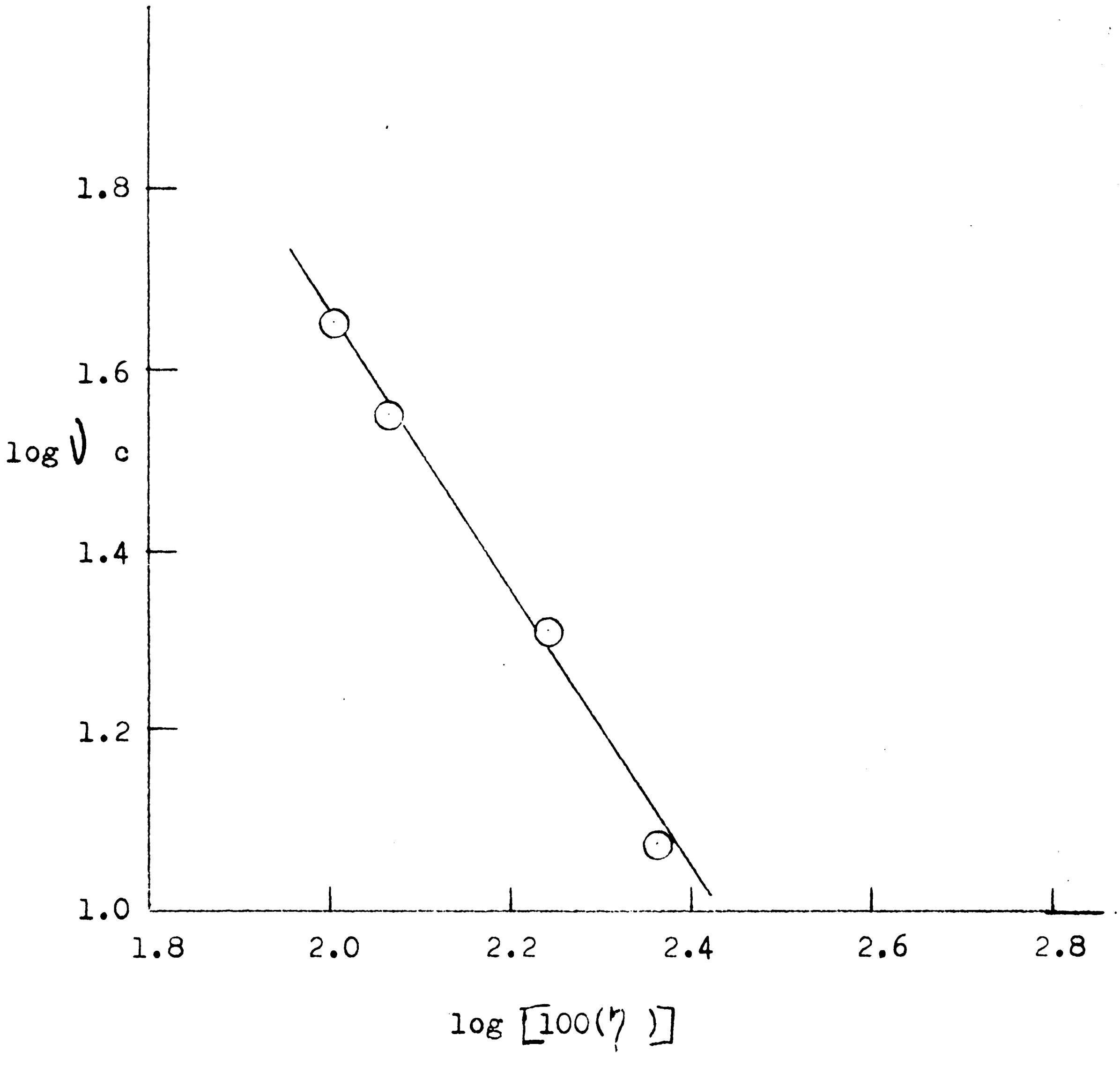


FIGURE 33. CRITICAL FREQUENCY VERSUS INTRINSIC VISCOSITY

n-Butyl Acetate



Condenser Method - It is a fact that the "dissipation factor is inversely proportional to the terminal total capacitance" (40). The obstacle in the measurement of high dielectric solvents has been as previously stated, that the dissipation factor is too large to be measured on the bridge. From the above quoted fact one should be able to increase the capacitance on each side of the bridge and lower the dissipation. This was attempted with a number of matched condensers.

Using large enough total capacity the dissipation should be reduced to such an extent that there should be no difficulty in measuring any solution desired. The .03 MFD condensers in the case of n-butyl acetate are withdrawn at 10 Kc and the measurement is accomplished with no difficulty with the bridge alone from this point. Below is a simplified diagram of the bridge and condensers.

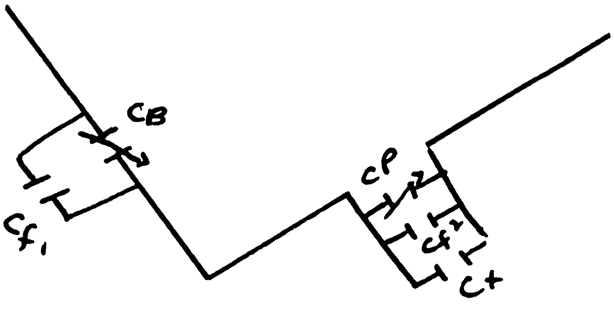


Figure 34

where Cf_1 and Cf_2 = two fixed condensers

In Table XVI and Figures 27, 28, 35, and 36 are shown the results of ethyl cellulose in n-butyl acetate solvent. Two important conclusions may be drawn from these results. These findings check those obtained with n-butyl acetate by the network and a new avenue is opened for measurements of solvents with high dielectric constants. Further investigation of this sort will not be reported in this work but experimentation is already underway by another investigator on this problem.

FIGURE 35. CONCENTRATION VERSUS CRITICAL FREQUENCY

CONDENSER METHOD

n-Butyl Acetate Solvent

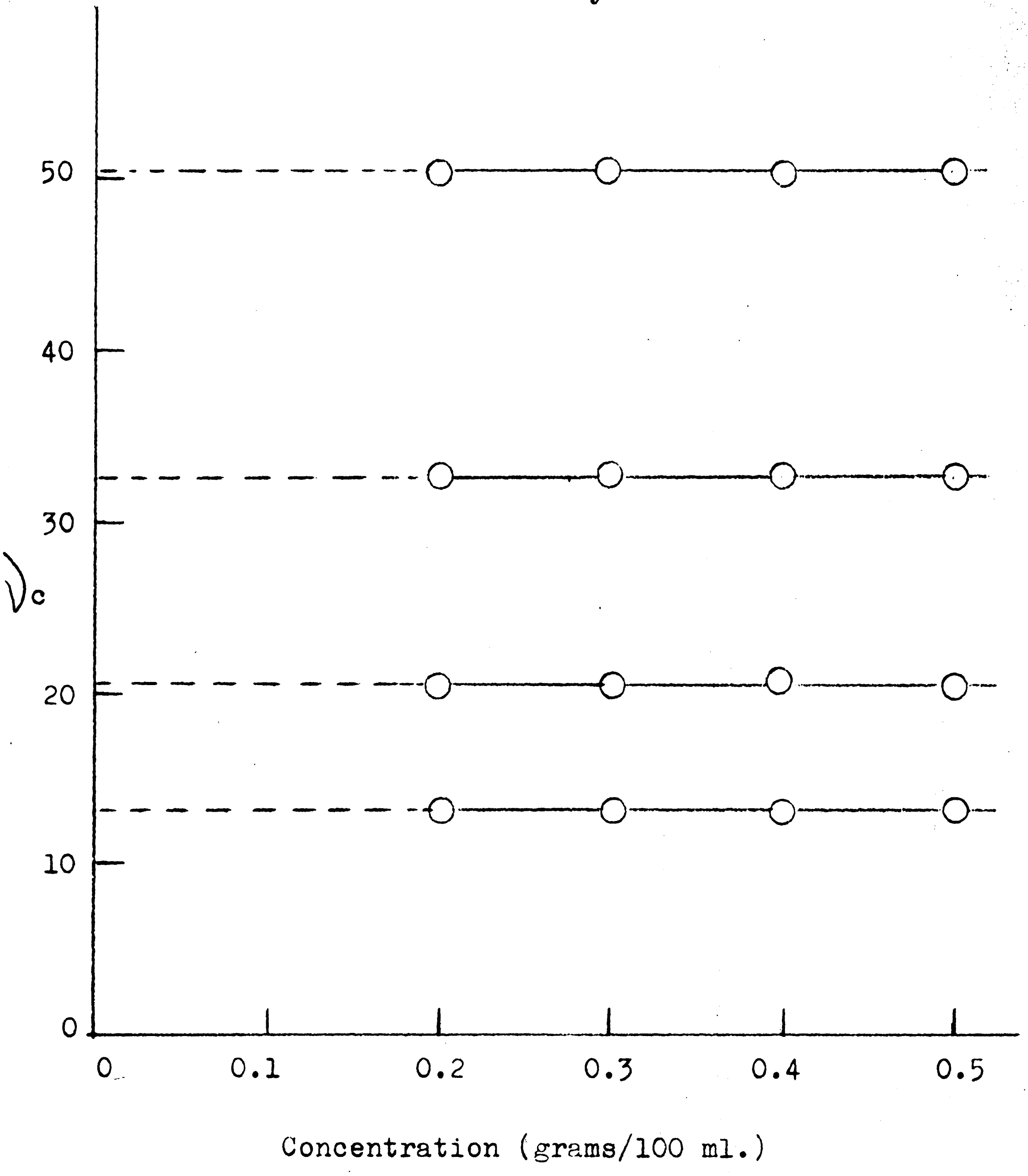
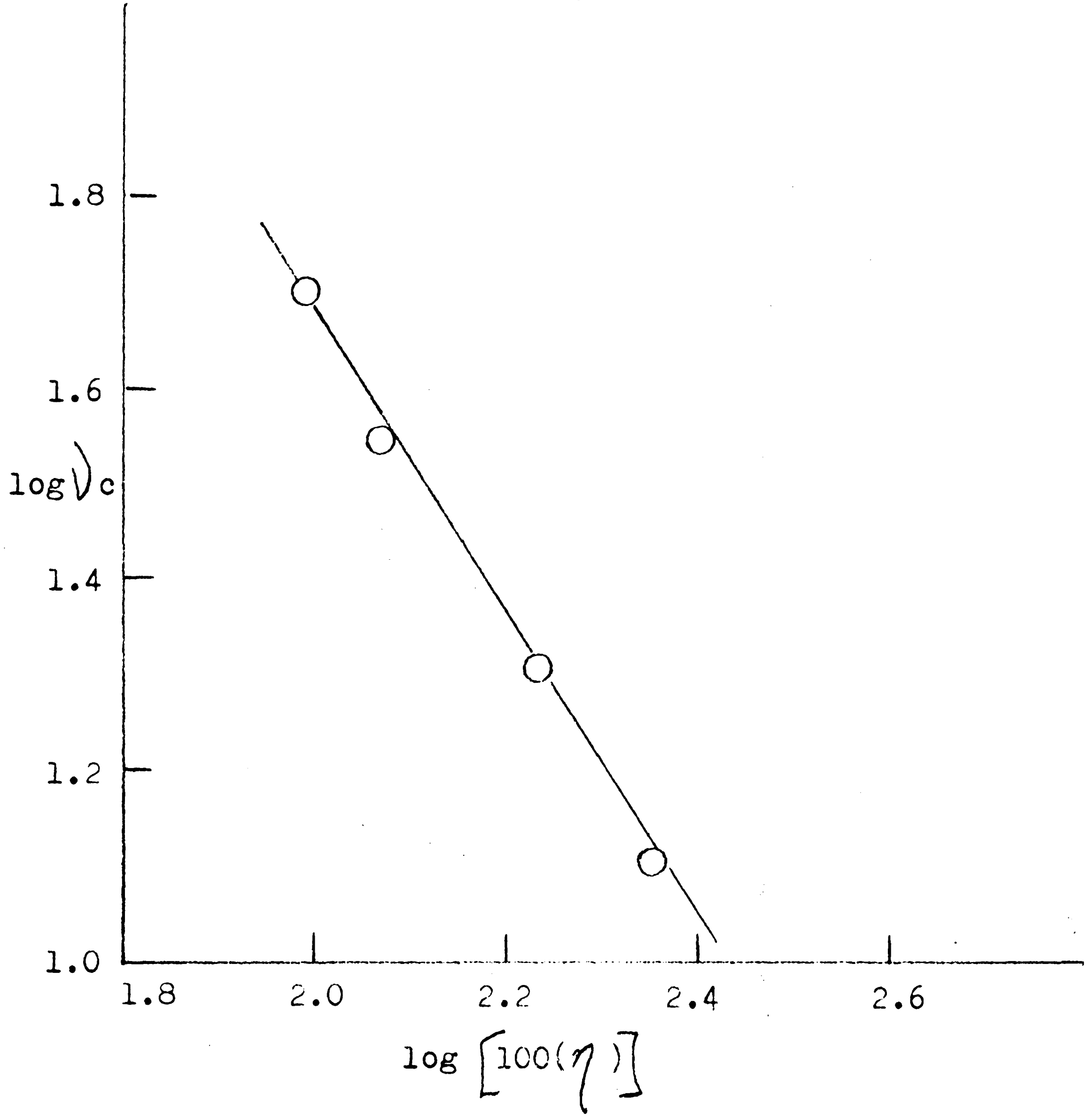


FIGURE 36. CRITICAL FREQUENCY VERSUS INTRINSIC VISCOSITY

CONDENSER METHOD

n-Butyl Acetate



DISCUSSION OF RESULTS

DISCUSSION OF RESULTS

From results obtained in the experimental section of this work the most striking seem to be the speed of the molecular weight determination as well as the applicability over the range of solvents since previously no method existed that could yield molecular weight of a fraction in ten minutes. The method here reported can do this with only a small margin of error. Now that the problem of working with solvents of high dielectric constant may be solved, new avenues should be opened. Molecular weights can be determined and the method may be used widely as a control technique. Of course, each solvent will present its own problems but with a suitable general method established these will be only minor and of a simple nature.

In the Literature Review section of this work molecular weight methods were discussed. Methods were divided into three groups, weight average, number average and viscosity average. The dielectric dispersion method may be shown to be similar to the viscosity average method in the following manner (72):

$$\Delta\epsilon = \Sigma\Delta\epsilon_i \qquad \partial_c = aM^b$$

$$\partial_c = \frac{\Sigma\Delta\epsilon_i C_i}{c} \qquad \Sigma\Delta\epsilon_i C_i = a'\Sigma c_i M_i$$

if $b=1$

$$\partial_c = \frac{b\,\Sigma\Delta\epsilon_i C_i}{c} \qquad \Sigma\frac{\Delta\epsilon_i c_i}{c} = \frac{a'\Sigma c_i M_i}{c}$$

$$= a'\bar{M_w}$$

where ϵ = dielectric

ν_c = critical frequency

C = capacity

$\bar{M}_w$ = weight average molecular weight

a, a' & b = constants

When b = 1, which is the more usual case, the molecular weight would be an average somewhere between the number and weight average. This is quite similar to the viscosity average.

Distribution Curves

Distribution curves were also discussed briefly in an earlier section. The original purpose of this research was to relate distribution curves with dielectric dispersion curves. No specific work has been done regarding this in this investigation but some interesting observations were made. It is quite obvious when dielectric dispersion is plotted versus the log of the frequency that the curves are different, depending on the fraction. For example, if a high molecular weight sharp fraction is plotted, a curve is obtained that resembles that shown below (Figure 37). A sharp fraction of moderate molecular weight and a sharp fraction with low molecular weight are plotted below (Figures 37a and 37b). Possibly of more interest is the case when the average molecular weight of an original material (Figure 37c) is approximately the same as that of the sharp fraction of moderate molecular weight (Figure 37a). A very marked difference can be noted between the broad and narrow distribution curves. There should be an excellent possibility of relating distribution curves obtained from fractionation and from dielectric dispersion. After a material has been fractionated the distribution curve possibly may be very quickly obtained from a dielectric investigation.

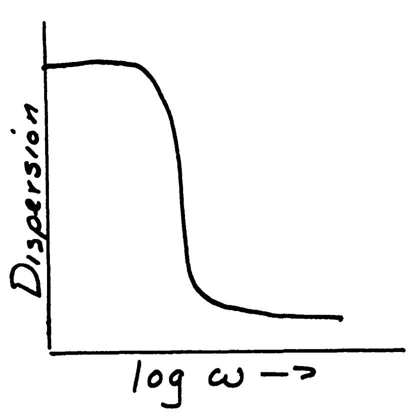


Figure 37

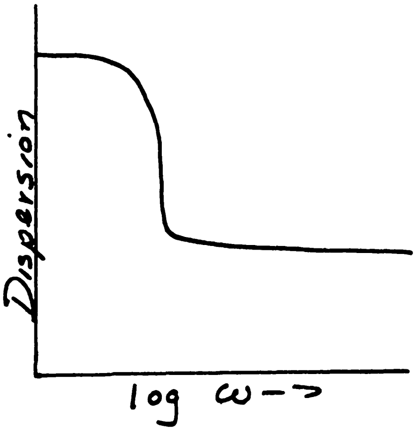


Figure 37a

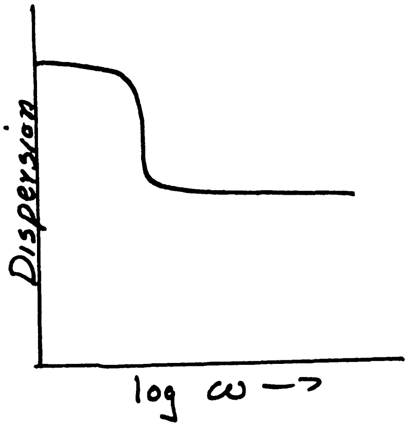


Figure 37b

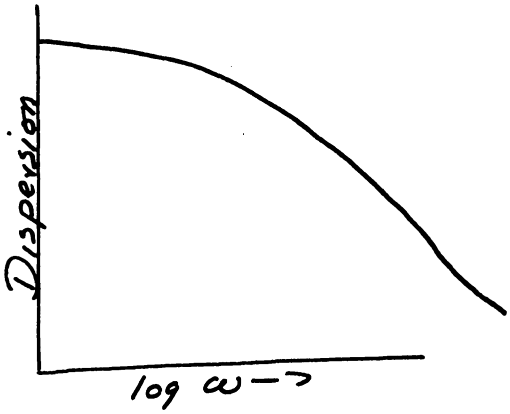


Figure 37c

Heat Treatment of Samples

The necessity of heat treatment of the solutions appears to be a consequence of the solvents employed. With cellulose acetate in dioxane (46) this was not necessary. This would lead one to the conclusion that dioxane is a better solvent for cellulose acetate than for ethyl cellulose but, in fact, no solvent that was employed in this investigation could be used unless heat treatment was employed. The heat treatment appeared to enable the solvent to completely disperse the polymer so as to obtain a true solution. For the solvent to enter between the individual chains some additional force such as heat was needed. This conclusion, that the solvent at room temperature had not completely dispersed the polymer, is strongly supported by the fact that with little or no oven treatment the fraction exhibited a lower critical frequency than with a reasonable period of oven treatment. The established relation between critical frequency and molecular weight shows that the higher the molecular weight, the lower the critical frequency. This would appear to indicate that the sample being measured with no oven treatment had not been dispersed to individual chains but existed much more like micellar structures in dispersion.

Observed Difference in Capacitance Drop

With cellulose acetate in dioxane, dilute solutions showed a drop of about 0.5 - 1.0 micro microfarads. Ethyl cellulose in dioxane and the other four solvents employed for the same concentration exhibited a drop of 5.0 - 6.0 micro microfarads. No explanation can be offered for such a phenomena as some fault can be found with each postulate. The difference in the state of the cellulose polymers dissolved in the solvents would certainly seem to offer a possibility. There is a possibility that ethyl cellulose in dioxane is more solvated than cellulose acetate in dioxane and if so, this solvated particle might have a greater resistance to rotation in the field. The observed necessity for oven treatment would somewhat contradict this postulate. Such phenomena as differences in dipole moment, difference in molecular weight, degree of solvation of the ester and ether linkages of the above polymers and dipole-dipole interaction must be considered in explanation.

Dispersion Region

There is quite a difference in the dispersion region for ethyl cellulose as compared to that found for cellulose acetate which extended only up to 100 Kc. A second dispersion region began at higher frequencies and continued beyond 400 Kc. However, ethyl cellulose dispersion commences at approximately the same frequency, 600 cycles to 1 Kc, and continues to 300 Kc - 400 Kc. The only explanation must again lie in the difference in the state of the polymer molecule.

Concentration versus Critical Frequency

With dioxane, carbon tetrachloride, and n-butyl acetate the critical frequency was concentration independent. However, with benzene and toluene the critical frequency was dependent upon concentration. It is possible to speculate concerning this phenomena with regard to a possibility of hydrogen bonding. Benzene and toluene are the only solvents that did not possess a group or groups that are capable of hydrogen bonding with the polymer molecule. The former three are all capable of forming hydrogen bonds. It would seem then that some form of association between polymer and solvent could occur in these solvents so that a possible explanation for the dependence on the concentration lie in this fact.

Assuming that association is present between the polymer and the solvent there would be only a slight possibility that chains would be entangled. The solvents dioxane, carbon tetrachloride, and n-butyl acetate would tend to destroy almost all possibilities of secondary forces holding the different chains together in an aggregate. Instead of the secondary forces existing between chains, they would be holding polymer and solvent into a highly solvated molecule. With the solvents that hydrogen bond, the polymer molecule would be separate and individual. No concentration dependence would be noticed since at the various concentrations used there would be little chance for polymer-polymer interaction and thus all molecules would be of essentially the same size.

With benzene and toluene the reverse would be true. Since they are both unable to form hydrogen bonds, some secondary forces would be free and capable of forming bonds between chains. This would then lead to an aggregation of chains or a micellar structure. As the concentration is increased the chance for such an aggregation is more possible. It is known that the larger the molecule, the lower the critical frequency. With increasing concentration the molecule would become larger and exhibit a lower critical frequency. In each case above, this was the observed behavior, corresponding with the postulate.

Failure of Glass-covered Electrodes to Produce Acceptable Results

The work with the glass cell yielded no acceptable results as was shown previously. This could be due to the fact that all factors of the entire situation were not considered. As was shown in the last section of this work, the calculated capacitance included the capacitance of the air and glass. There is reason to believe that a thin film of air exists between the glass and the metal electrode. If this would be considered and represented by Cx, the total capacitance would be

$$\frac{1}{C_{measured}} = \frac{1}{C_g} + \frac{1}{C_x} + \frac{1}{C_a}$$

where Cg = capacity of glass

Ca = capacity of air

Ca and Cg would be large compared with Cx. The reciprocal of this value would be large and would have a very pronounced effect upon the calculated capacity of the cell. The problem arises as to the measurement of Cx so the correct Cmeasured may be obtained. To date no suitable method of measurement has been found.

The above may not be the complete solution to the problem but such a problem can be shown to exist. Water, which exhibits a dielectric constant of approximately 80 by the above method of determination, showed a dielectric constant of 6.0 - 7.0. Besides water, n-butyl alcohol and ethylene chloride exhibit false values.

Type of Dispersion Noted

The question arises as to what type of absorption was exhibited with ethyl cellulose in the various solvents employed. The literature to date deals almost exclusively with resonance absorption and Debye's absorption, and much of the work in the literature on proteins as well as solid polymer shows agreement with Debye's theory.

For a comparison to be made of the dielectric dispersion phenomena in this investigation with that of Debye, the $\frac{\epsilon - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty}$ versus frequency curves must be compared. For Debye's absorption, equation (1) for one relaxation time should be:

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

where $\tau = \frac{1}{2\pi fm}$

fm = frequency at the maximum slope

A comparison can be made (Figure 38 and Table XIX) between the Debye curve calculated from equation (1) and ethyl cellulose (F-1) in dioxane. In this case "fm" was chosen to be 6.5 Kc from Table XVI. The 6.5 was the critical frequency determined by measurement and represents the point of maximum slope of the dispersion curve.

It is apparent from this graph that the experimental dispersion region occurs in a region of frequencies comparable with that of Debye's but somewhat broader. It should be pointed out that the Debye curve assumes the presence of only one relaxation time. This fact is not strictly in accordance with conditions known to exist in ethyl cellulose due to the fact that even sharp fractions show some heterogeneity with respect to chain lengths. The graph does point out however that there is not too wide a variance in relaxation times and that the fraction is not too broad in its distribution of chain lengths.

A similar plot was made on cellulose acetate in dioxane and results were also in accordance with the above. This graph is not included in this discussion.

On the basis of the similarity between the two curves, one must assume that the experimental dispersion is that of the Debye type.

FIGURE 38. COMPARISON OF DEBYE AND EXPERIMENTAL DISPERSION

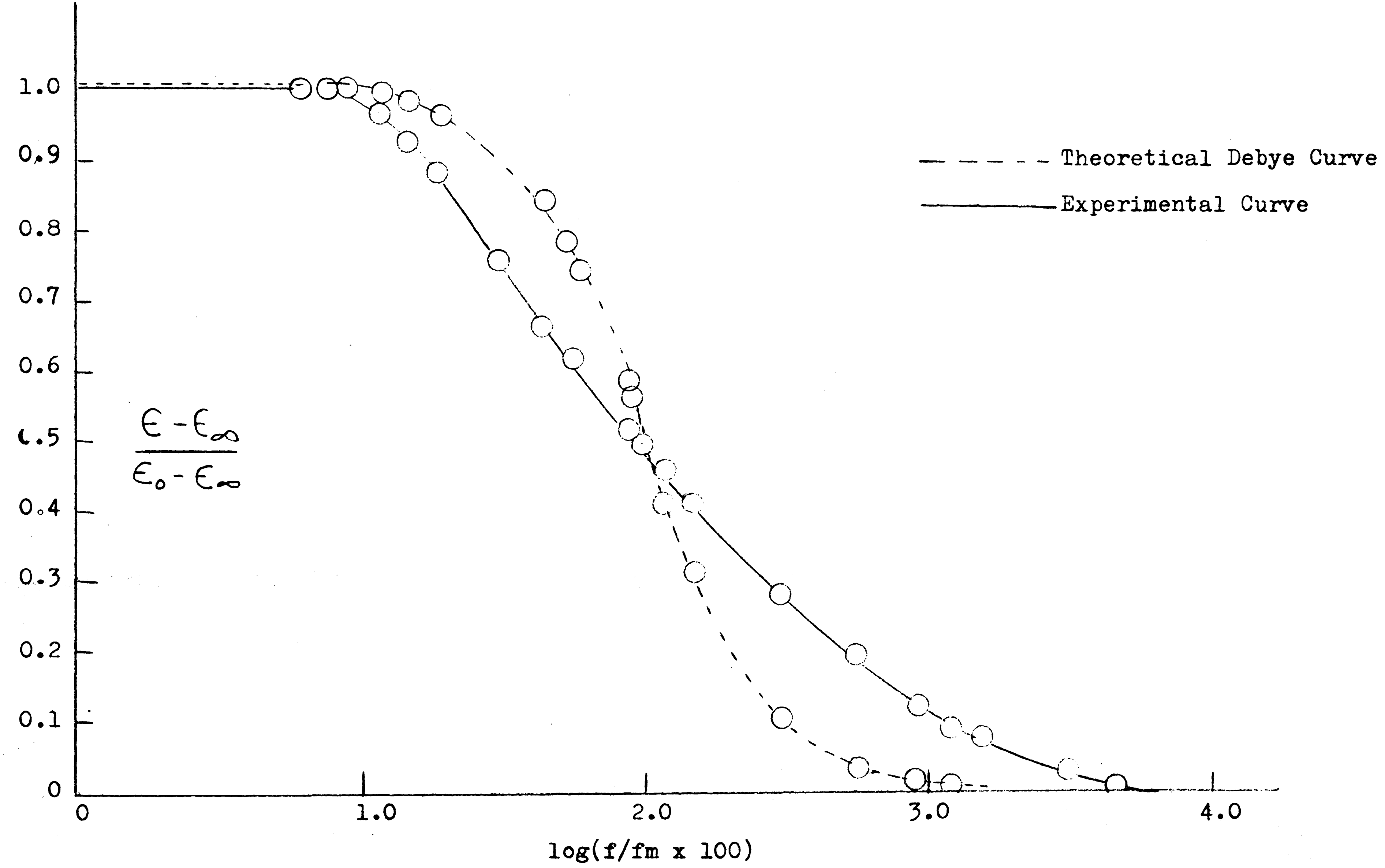


TABLE XIX

CALCULATION OF THEORETICAL DEBYE DISPERSION USING MAXIMUM SLOPE AS 6.5 KC

Frequency	f/fm	log(f/fm x 100)	$(f/fm)^2$	$\frac{1}{1 + (f/fm)^2} = \frac{\epsilon - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty}$	Exp $\frac{\epsilon - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty}$
400 cps	0.059	0.77	0.003	1.00	1.00
500 cps	0.074	0.87	0.005	1.00	1.00
600 cps	0.088	0.94	0.008	1.00	1.00
800 cps	0.118	1.07	0.014	0.99	0.963
1 Kc	0.147	1.17	0.02	0.98	0.925
3 Kc	0.44	1.64	0.19	0.84	0.657
4 Kc	0.59	1.77	0.35	0.74	0.617
6 Kc	0.88	1.94	0.78	0.56	0.522
8 Kc	1.18	2.07	1.39	0.41	0.458
10 Kc	1.47	2.17	2.15	0.31	0.411
20 Kc	2.94	2.47	8.60	0.10	0.280
35 Kc	5.15	2.71	26.5	.03	0.190
60 Kc	8.82	2.94	78.0	.013	0.120
80 Kc	11.76	3.07	138.0	.007	0.090
100 Kc	14.70	3.17	215.0	.005	0.076
200 Kc	29.41	3.47	863.0	.001	0.031
300 Kc	44.11	3.64	1942.0	.0005	0
340 Kc	50.00	3.70	2500.0	.0004	0
380 Kc	55.88	3.75	3120.0	.0003	0
400 Kc	58.82	3.76	3460.0	.0002	0

Resonance absorption can be disregarded since the characteristic difference is the narrowness of the dispersion curve. If the figure below is consulted, the difference is immediately apparent. The resonance absorption region varies from an extremely narrow one when $\omega_0 \tau >> 1$ to one in which the width is equal to that of Debye's when $\omega_0 \tau << 1$.

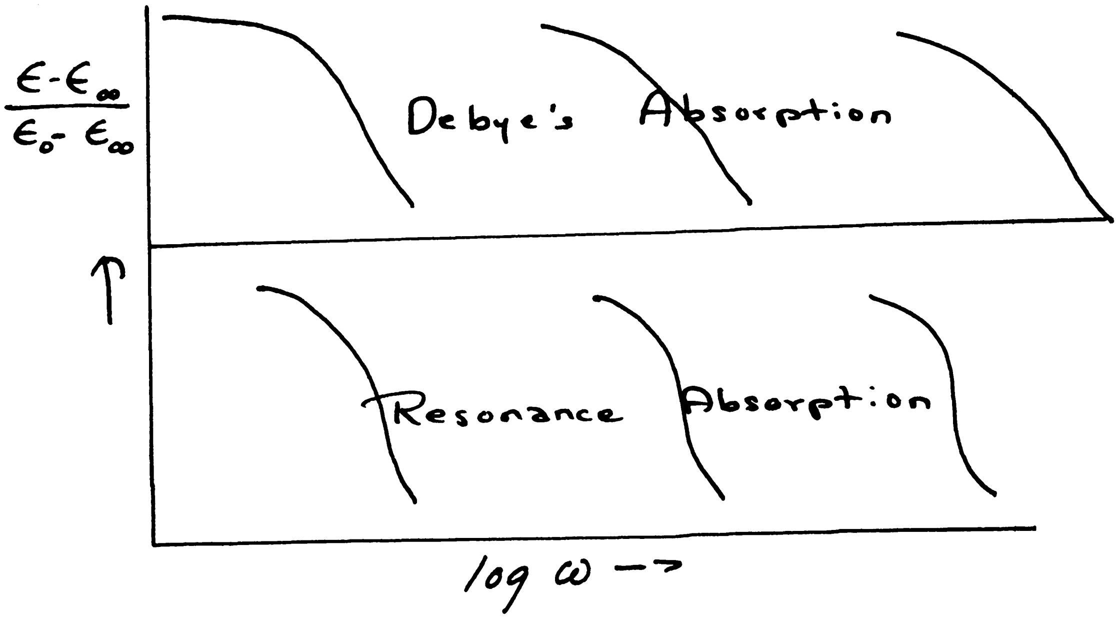


Figure 39

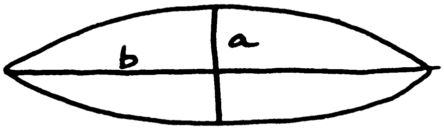
Shape and Nature of Particle in Solution

It would appear that for a better understanding of the phenomena observed in this investigation the nature of the particle in solution should be understood. Unfortunately the author can give no clear picture of the shape but can only make postulates.

As was previously mentioned regarding cellulose derivaties, the chain is either a stiffened coil or flexible rod like structure, depending on the molecular weight. Assuming the ethyl cellulose in this investigation is of the stiffened coil nature, it might be pictured in the following manner:

Earlier evidence pointed out that there was two dispersion regions present with ethyl cellulose in dioxane as well as all other solvents investigated. This may be explained by a number of possible means.

One such means would be that of considering the dissolved particle as an ellipsoid of revolution. The decrease in the dielectric constant may be related to the alignment taking place along the two different axes, "a" and "b", of the ellipsoid.



The low frequency dispersion region would involve what may be termed as oscillations about the major axes "b" of the ellipsoid. The decrease in the dielectric constant associated with the higher frequencies involves an oscillation or rotation about the minor axes "a". This continues to a point where oscillations of the ellipsoid do not occur due to the high frequency of the electrostatic field, after which point there should be no contribution to the dielectric constant of the solution due to the dissolved polymer molecule except the existence of atomic or electronic polarization.

In a much less plausible but easily understandable example, the model of the dissolved polymer may be assumed to be a rigid rod. In a consideration of the phenomena taking place the low frequency dispersion region would correspond to an end over end rotation of the entire chain. The higher frequency region would be the transverse rotation of the chain.

The former possibility would be more plausible but as a simple explanation the latter might be considered. There must be other explanations which would perhaps be equally as satisfactory. The author does not in any way claim the above to be absolutely valid as there may be a combination of phenomena rather than a single one.

The cause for a chain or ellipsoid oscillating or rotating in an alternating field should be shown. The polymer molecules in this investigation and others reported in the literature section possess some degree of polarity. Some possess more than others and to date no work is known regarding non polar molecules in solution.

The fact is well understood that negative and positive charges will orient from one pole to another if an alternating field be applied. The diagram below would be the reverse after one oscillation of the field.

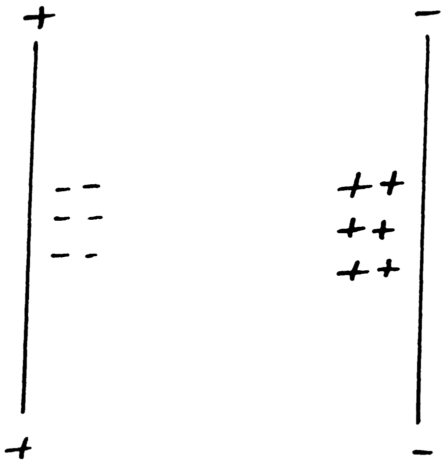


Figure 40

If then a polymer chain with one end positive and the opposite negative were placed between two plates and an a.c. field were applied, the chain would in some way oscillate with the field. A point would soon be reached in which rotation of the entire chain could not be possible and beyond this point the second dispersion would commence. This region as previously mentioned was not investigated. Such an explanation does not seem to be entirely plausible but if the chain were considered to be composed of segments, the reasoning should be more accurate (71).

If the chain below were considered when a field was applied, the units or segments would act so as to cancel out its neighbor.

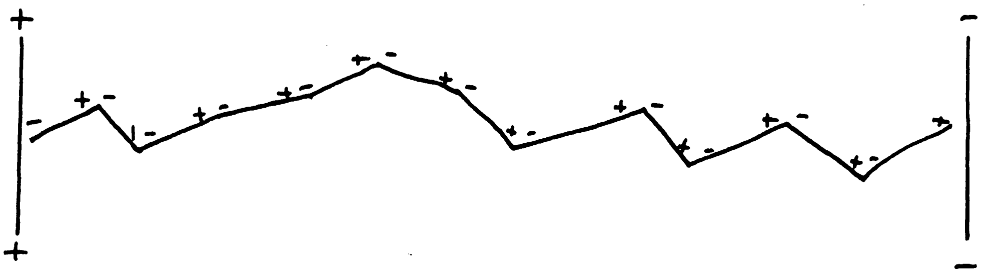


Figure 41

With the positive and negative charges opposing and nullifying each other, the charges on the end of the chain would be acting or oscillating in the field. Also this high frequency region might possibly be due to a segment in the chain oscillating.

With dilute solutions the chains should behave essentially without interference from others. There is always the possibility, however, that there is some entanglement. This possibility becomes more probable as the number of polymer molecules is increased. In the latter case and to some small extent in the former the situation might be pictured as polymer chains in an entangled fashion.

The question would then arise as to how the chains would show any molecular weight dependence. If a chain entangled with others were to be considered, there is no reason to believe that the free ends would not oscillate even though the chain would not be independent of the surrounding chains. The free ends must be influenced to some extent by the middle of the chain. One must not envision the chains laying flat on one another but in three dimensions. There would be contact but not to the extent that the entire length would not in some way influence the behavior of the ends of the chain.

Much can be learned also from a study of dielectric dispersion at different temperatures. Although this was not investigated in this work, it has been in others (89)(115).

If the above, concerning oscillation of the chains, be accepted as the picture of behavior in solution, high polymers should show a molecular weight dependence. This is true, as was previously pointed out, since the chains will follow the frequency until they are forced to drop out because of their length. This seems reasonable since the first dispersion region is narrower than the second. If longitudinal rotation, segment rotation, or side chain rotation were taking place, then the second would of necessity be broader.

Again it should be emphasized that the author does not claim the above discussion absolutely valid. There must be numerous possibilities and for a completely accurate picture a combination of all should be considered.

Effect of Degree of Substitution

The ethoxy content, as far as the investigation can determine, has no effect on the critical frequency. The D.S. range is limited by the solvent. The solvents that were investigated would not dissolve ethyl cellulose with an ethoxy content that varied markedly from that used throughout the investigation. A variation of one or two percent above or below showed no effect on the critical frequency for the same molecular weight material.

The measurement below was not included in the experimental section but an original material of D.S. 47.6% was roughly fractionated to obtain an $[\eta]$ of 3.03 which corresponded to a sharp fraction of approximately the same

$[\eta]$. The (V_c) was approximately the same, considering the slight variation in the $[\eta]$, regardless of the D.S.

Fraction	D.S.	$[\eta]$	$[V_c]$
F-X	47.6	3.03	6.4
F-1	48.7	3.01	6.5

Electrode Polarization

As was mentioned the most difficult problem encountered in this investigation was the measurement of higher dielectric solvents and electrode polarization appears to be generally the cause for such problems. There can be no absolute proof with the limited amount of work accomplished as to whether the problem was electrode polarization or some other effect. Electrode polarization appears to be very plausible as it is most serious both in the frequency range in which the author worked and with solvents of high conductivity. As the frequency increases the effect diminishes with solvents of high conductivity. The four original solvents investigated were known to possess low conductivity.

Electrode polarization arises due to irreversible reactions taking place at the electrode and possibly caused by ionic impurities in solution or by nature of solvent employed.

Corrections for such sources may be made in quite a number of ways, all accomplishing the same results. The relation of Johnson and Cole (60) used in this work is one of many.

It would certainly seem possible that polarization was taking place in this work as evidenced and corrected by the use of such an equation. Such a phenomena as electrode polarization should be of no real concern if it can be treated by the proper equation. There is however the possibility of combined effects which might lead to difficulties not treated by the corrective measures.

Condenser Method

The "condenser" method may prove to be a breakthrough in the application of high dielectric solvents in dielectric dispersion method.

The method was proven to be accurate in two ways. In one experiment, F-6 ethyl cellulose in dioxane, the critical frequency agreed to within 0.1 Kc. of the value previously obtained by a differential procedure. Fraction 8 was also investigated in the same manner and no difference was noted in the critical frequencies obtained.

In the second set of experiments all of the fractions used by the condenser method were in agreement with the "network" method previously used with ethyl cellulose in n-butyl acetate. The "network" method had previously been proven to be acceptable by measurement of ethyl cellulose in dioxane and benzene.

This appeared to indicate that the "condenser method" could be applied to solvents of high dielectric constant. Of course in each case preliminary investigations will be necessary for any new system. The values of the condensers in parallel with the bridge will have to be adjusted in certain instances as well as the amplification required.

Molecular Weight from Dielectric Dispersion

This work was not the first that has shown a relation to exist between dielectric dispersion and molecular weight (46)(114)(115). In two of these measurements doubt existed as to accuracy of measurements, but there existed a very definite relationship between molecular weight and the frequency of maximum absorption.

In the author's Master of Science work a very definite relationship for cellulose acetate in dioxane was found. A straight line which resulted from a plot of log critical frequency versus log Degree of Polymerization took the form

$$\log D.P. = 2.60 - 0.67 \log (\quad)$$

In regard to ethyl cellulose in the solvents investigated the same general relationship held. The equations are of the same form as above but contain constants slightly different from above. Tables XX and XXI show the equations for the five solvents investigated with respect to intrinsic viscosity as well as degree of polymerization.

TABLE XX

CORRELATION OF CRITICAL FREQUENCY AND INTRINSIC VISCOSITY FOR ETHYL CELLULOSE SOLUTIONS

Solvent	Equation
Dioxane	$\log(100[\eta]) = 2.97 - 0.59 \log[\nu_c]$
Carbon Tetrachloride	$\log(100[\eta]) = 3.41 - 0.83 \log[\nu_c]$
Benzene	$\log(100[\eta]) = 3.41 - 0.77 \log[\nu_c]$
Toluene	$\log(100[\eta]) = 3.23 - 0.65 \log[\nu_c]$
n-Butyl Acetate	$\log(100[\eta]) = 3.23 - 0.85 \log[\nu_c]$

TABLE XXI

CORRELATION OF CRITICAL FREQUENCY FOR D.P. FOR ETHYL CELLULOSE SOLUTIONS

Solvent	Equation
Dioxane	$\log P = 3.06 - 0.56 \log[\nu_c]$
Carbon Tetrachloride	$\log P = 3.46 - 0.82 \log[\nu_c]$
Benzene	$\log P = 3.46 - 0.72 \log[\nu_c]$
Toluene	$\log P = 3.35 - 0.64 \log[\nu_c]$
n-Butyl Acetate	$\log P = 3.40 - 0.70 \log[\nu_c]$

After having determined the equation for ethyl cellulose in a solvent, the molecular weight can be determined in a minimum of fifteen minutes. Moreover, the results are equally as accurate as any method existing today. As an example, a molecular weight can be reproduced by actual experiment to within ± 2.0% over a period of more than eighteen months. This was done on a number of occasions with entirely different bridge arrangements and methods with equally satisfactory results being obtained.

As soon as possible, light scattering results should be obtained that should lead to valuable information concerning root mean square end to end distance. From below the critical frequency is proportional to the root mean square end to end distance. This is shown by using the accepted relationships between intrinsic viscosity and root mean square end to end distance and between intrinsic viscosity and degree of polymerization.

$$\phi(\bar{r}^2)^{3/2} = [\eta]M - [\eta]\, P M_0$$

and

$$[\eta] = K M^a = K P^{a+1}$$

The above two equations may be related to give

$$(\bar{r})^{3/2} = A P^{a+1}$$

then

$$\log P = B + C \log(\bar{r}^2)$$

where A = $\phi K' M_0^{a+1}$

B and C = constants

The above equation indicates that the root mean square end to end distance is in some way proportional to the critical frequency. As soon as this relationship can be confirmed by actual results, a rapid method for determination of $(\hat{\gamma}^2)$ will exist. It would certainly seem reasonable to expect such a relationship to exist since the critical frequency determined by the dielectric dispersion method and the root mean square end to end distance are proportional. The γ_c is based on the length of the chains present as was discussed above.

Rapidity of measurement, as well as excellent reproducibility, are factors that one can never neglect in evaluating the merits of a molecular weight measurement. The claim is not made here that the method is ready for extensive applicability. Many problems will arise but with patience and persistance this method might well become an extremely valuable tool in high polymer chemistry.

CONCLUSIONS

CONCLUSIONS

1. A dielectric cell, containing a polymer solution, decreased in capacity over the frequency range of 400 cycles to 400 kilocycles due to the presence of the solution.

2. A second decrease in capacitance was observed but not investigated beyond 400 kilocycles.

3. The above decreases in capacitance must be due to the decrease in the dielectric constant of the solution, ethyl cellulose in various solvents. The drop cannot be attributed to a decrease in the solvent or air capacity and thus must be a consequence of the solute polymer molecules.

4. The first dispersion region may be explained by an end to end oscillation of the polymer molecules and the second region to possibly a transverse rotation.

5. The first dispersion region has a molecular weight dependence related to the critical frequency (ν_c) by general equation below:

   $$\log M.W. = B + C \log (\nu_c)$$

   where B and C are constants

   The critical frequency (ν_c) is the point at which the dispersion is fifty percent completed. It is found at the greatest slope of the dispersion curve.

6. The above described dispersion appears to be of the theoretical Debye type.

7. Ethyl cellulose appears to behave as a flexible rod which at high molecular weights tends to coil upon itself.

8. Dielectric dispersion curves may possibly be related to distribution curves obtained by fractionation. Broad or narrow distribution curves can be easily detected at this point of the investigation.

9. Solvents affect the critical frequency obtained. Benzene and toluene show a concentration dependence of the (ν_c) while dioxane, carbon tetrachloride, and n-butyl acetate do not. This phenomena can possibly be attributed to an association of the polymer and solvent.

10. High dielectric solvents may now be investigated by a "condenser" method. The measurement of high dielectric solvents was long a drawback to the dielectric dispersion method of molecular weight determination.

11. Molecular weights may be obtained very rapidly. This is the outstanding feature of the dielectric method.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Abadie, G., Charbonniere, R., Gidel A., Girard, P., and Guilbot, A., Compt. Rend. 241; 1137-39 (1955).
2. Adams, H. E. and Powers, P. O., Ind. Eng. Chem. (Anal. Ed.) 15; 711-14 (1943).
3. Alfrey, T., Bartovics. A., and Mark, H., J.A.C.S. 65; 2319 (1943).
4. Badger, R. M. and Blaker, R. H., J. Phys. and Col. Chem. 53; 1056-69 (1949).
5. Bartovics, A. and Mark, H., J.A.C.S. 65; 1901 (1943).
6. Bawn, C. E. H., "The Chemistry of High Polymers", Interscience Pub., Inc., New York, New York (1948).
7. Baxendale, J. H., Bywaters, S., and Evans, M. G., J. Poly. Sci. 1; 237 (1946).
8. Brice Phoenix Light Scattering Manual, Phoenix Precision Instrument Company, Philadephia 40, Pennsylvania.
9. Bridgeman, W. D., J.A.C.S. 60; 530 (1938).
10. Burk, R. E. and Grummitt, O., "The Chemistry of Large Molecules", Interscience Pub., Inc., New York, New York (1943).
11. Carter, W. C., Magat, M., and Schenider, W. C., Trans. Faraday Society 42A, 213-20 (1946).
12. Chemstrand Corporation, Decatur, Alabama, unpublished work.
13. Cole, K. S. and Cole, R. H., J. Chem. Phys. 9; 341-51 (1941).

14. Cole, K. S. and Curtis, H. J., Rev. Sci. Inst. 8; 333 (1937).

15. Cole, R. H., Rev. Sci. Inst. 9; 272 (1938).

16. Ibid, 12; 298 (1941).

17. Collie, C. N., Hasted, J. B. and Retson, D. M., Proc. Phys. Soc. (London) 60, 71-82 (1948).

18. Cragg, L. H. and Hammerschlag, H., Chem. Reviews 39; 80 (1946).

19. Crowe, R. W. and Smyth, C. P., J.A.C.S. 73, 5401-6 (1951).

20. Daniels, F., Mathews, J. H. and Williams, J. W., "Experimental Physical Chemistry", 3rd Edition, McGraw-Hill Book Co., New York, New York (1941).

21. DeBrauchere, L., Buess, D., Versluys, J., and DeBoch, J., Industre Chem. Belge 20; 356-7 (1955).

22. DeBrouchere, L., Buess, D., DeBoch, J., and Versluys, J., Bull. Soc. Chem. Belge 64; 669-95 (1955).

23. DeBrouchere, L., Van Beek, L. K. H., Rec. trav. chem. 75; 355-70 (1956).

24. Debye, P., Ber. 15; 777 (1913).

25. Debye, P. Trans. Faraday Soc. 30; 679 (1934).

26. Debye, P. and Bueche, F., J. Phys. and Col. Chem. 55; 235-8 (1951).

27. Deutsch, K., Wolf, E. A., Reddish, W., J. Poly. Sci. 13; 565 (1954).

28. The Dow Chemical Company, Midland, Michigan, unpublished work.

29. Drude, P., Z. Physik Chem. 23; 267 (1897).

30. Duclaux, J. and Wellman, E., Bull. Soc. Chim. (4) 27; 44 (1920).

31. Ibid, 414-20 (1920).

32. Elliott, M. A. and Williams, J. W., J.A.C.S. 61; 718 (1939).

33. Erbring, H. and Takei, M., Kolloid-Z. 96; 336-340 (1941).

34. Evans, H. C. and Young, D. W., Ind. Eng. Chem. 34; 461-6 (1942).

35. Flory, P. J., "Principles of Polymer Chemistry", Cornell University Press, Ithaca, New York (1953).

36. Franeau, J. and Burmbaum, G., J. Applied Phys. 20; 817-18 (1949).

37. Funt, B. J. and Mason, S. G., Can. J. Chem. 28B; 182-93 (1950).

38. Funt, B. L. and Sutherland, T. H., Can. J. Chem. 33; 1669 (1955).

39. Fuoss, R. M., J.A.C.S. 60; 451 (1938).

40. General Radio Catalog "O", General Radio Company, Cambridge, Massachusetts, p. 149.

41. Gilkerson, W. R., J. Chem. Phys. 27; (1957).

42. Girard, P., Abadie, P. and Charbonniere, R., J. Chim. Physique 47; 601-5 (1950).

43. Hague, B., "Alternating Current Bridge Methods", Pitman, London, England, (1932), p. 241 ff.

44. Hammerle, W. G. and Kirkwood, J. G., J. Chem. Phys. 23; 1743-9 (1955).

45. Ibid, 24; 1277 (1956).

46. Hawkins, M. C., Master of Science Thesis, V.P.I. (1956).

47. Haworth, W. N. and Machemer, H., J. Chem. Soc.; 2372 (1932).

48. Haynes, D. and Hunter, W. L., unpublished work.

49. Hennelly, E. J., Heston, W. M. and Smyth, C. P., J.A.C.S. 70; 4102 (1948).

50. Herzog, R. O., J. Chem. Phys. 30; 457 (1926).

51. Hess, K., Trogus, C., Evthing, P., Garthi, L., Ann. 506; 278-9 (1933).

52. Hess, K. Trogus, C., and Schwarshopf, C., Z. physik Chim. A162; 189 (1932).

53. Heuser, E., "The Chemistry of Cellulose", John Wiley & Sons, Inc., New York, New York (1950).

54. Hill, H. C., Rev. Sci. Inst. 29; 224 (1952).

55. Hill, R. A. W. and Sutton, L. E., J. Chem. Soc.; 1482 (1953).

56. Huggins, M. L., J. Chem. Phys. 9; 440 (1941).

57. Iacoviello, J. C., Master of Science Thesis, V.P.I., (1951).

58. International Critical Tables, Vol. VI, McGraw-Hill Book Co., Inc., New York, New York.

59. Ishidate, M. and Kamura, Y., Chemical Abstracts 51; 10141a (1951).

60. Johnson, J. F. and Cole, R. H., J.A.C.S. 73; 4536 (1951).

61. Karner, P. K., Z. Angew. Chim. 37; 1003 (1924).

62. Kirkwood, J. G., J. Chem. Phys. 7; 911 (1939(.

63. Kirkwood, J. G., Trans. Faraday Soc. 42A; 7 (1946).

64. Kirkwood, J. G., Rec. Trav. Chim. 75; 355-70 (1956).

65. Kraemer, E. O., J. Phys. Chem. 39; 153 (1935).

66. Kuhn, W. and Kuhn H., Helv. Chim. Acta. 26; 1394 (1943).

67. Kuhn, W., Kolloid-Z 68; 2 (1934).

68. Ibid, 76; 258 (1936).

69. Lawrence, W. C., Bachelor of Science Thesis, V.P.I. (1958).

70. Lawson, H. W., Rev. Sci. Inst. 12; 298 (1941).

71. Levi, D. W., Hunter, W. L., and Hawkins, M. C., personal discussion.

72. Levi, D. W., personal communication.

73. Lewis, C. W. and Hagle, D. H., J. Poly. Sci. 21; 411 (1956).

74. Lorand, E. J., Ind. Eng. Chem. 31; 891 (1939).

75. Lovell, E. L. and Hebbert, H., J.A.C.S. 63; 2070-2 (1941).

76. Malsch, J., Physik Z. 33; 19 (1932).

77. Mark, H., J. Phys. Chem. 44; 779 (1940).

78. Martin, G., Physik Z. 37; 665 (1936).

79. McNeer, R. D., Master of Science Thesis, V.P.I. (1948).

80. McNeer, R. D., Ph.D. Thesis, V.P.I. (1949).

81. Meyer, K. H., "Natural and Synthetic High Polymers", High Polymer Series, Vol. IV, Interscience Pub., Inc., New York (1942), pp. 241-3.

82. Mikhailov, G. P., Borisova, T. I. and Dmitrochenko, D. A., Zhur. Tekh. Fig. 26; 1924 (1956).

83. Monier-Williams, J. Chem. Soc. 119; 804 (1921).

84. Offergeld, G., Nature 178; 1460-1 (1956).

85. Okamura, I., Cellulosechem 14; 135 (1933).

86. Oncley, J. L., J.A.C.S. 60; 1115 (1938).

87. Oncley, J. L., J. Phys. Chem. 44; 1103 (1940).

88. Oncley, J. L., Chem. Reviews 30; 433 (1942).

89. Oncley, J. L., "Proteins, Amino Acids and Peptides", Chap. 22, Rheinhold Publishing Co., New York, New York (1943).

90. Onsager, L., J.A.C.S. 58; 1486 (1936).

91. Ott, E., "Cellulose and Cellulose Derivatives", Vol. V, Interscience Publishers, Inc., New York, New York (1954).

92. Pauley, J. L. and Testerman, M. K., J. Poly. Sci. 21; 437-53 (1956).

93. Polson, A., Kolloid-Z. 83; 172 (1938).

94. Reddish, W., Trans. Faraday Soc. 46; 459-75 (1950).

95. Scheiber, D. J. and Mead, D. J., J. Chem. Phys. 27; 326 (1957).

96. Scherer, P. C. and Iacoviello, J. G., Rayon and Synthetic Textiles 32, No. 11; 47 (1951).

97. Scherer, P. C., Levi, D. W. and Hawkins, M. C., J. Poly. Sci. 24, 19 (1957).

98. Scherer, P. C. and Masuelli, F. J., Rayon and Synthetic Textiles 30, No. 2 (1949).

99. Scherer, P. C. and McKeer, R. D., Rayon and Synthetic Textiles 30, No. 8; 56 (1949).

100. Scherer, P. C. and Testerman, M. K., J. Poly. Sci. 7; 549-65 (1951).

101. Schmelzer, C., Physik Z. 37; 162 (1936).

102. Schmidt, A. X. and Marlies, C. A., "Principles of High Polymer Theory and Practice", McGraw-Hill Book Co., Inc., New York, New York (1948) pp. 235-56.

103. Schulz, G. V., Physik Z. B46; 137 (1940).

104. Smyth, C. P., "Dielectric Behavior and Structure", McGraw-Hill Book Co., Inc., New York, New York (1955) pp. 211-213.

105. Spurlin, H. M., J.A.C.S. 61; 2222 (1939).

106. Stacey, K. A., "Light Scattering in Physical Chemistry", Academic Press, Inc., New York, New York (1956), pp. 90-92.

107. Staudinger, H., "Die Hochmolekularen Organischen Verbindungen", J. Springen, Berlin (1932) p. 457.

108. Staudinger, H., Ber. 67; 96 (1934).

109. Staudinger, H., Papie Fahr. 36; Tech-Wiss. Tl., 381-8 (1938).

110. Staudinger, H., and Reinecke, F., Ann. 535; 47 (1938).

111. Stein, R. S. and Doty, P., J.A.C.S. 68; 156-67 (1946).

112. Strella, S. and Zand, R., J. Poly. Sci. 25; 97-104 (1957).

113. Ibid; 105-114 (1957).

114. Testerman, M. K., M. S. Thesis, V.P.I. (1947).

115. Testerman, M. K., Ph.D. Thesis, V.P.I. (1950).

116. Thompson, R. B., M. S. Thesis, V.P.I. (1950).

117. Thorton, W. M., Proc. Roy. Soc. (London) 82; 422 (1909).

118. Union Carbide Company, Charleston, West Virginia, unpublished work.

119. VanArkel, A. E. and Snoek, J. L., Trans. Faraday Soc. 30; 707 (1934).

120. Voet, A., J. Phys. and Colloid Chem. 53; 597 (1949).

121. Wyman, J., J.A.C.S. 58; 1482 (1936).

122. Wyman, J., Phys. Rev. 35; 623 (1930).

123. Wyman, J. and Marcy, H. O., J.A.C.S. 63; 3388 (1941).

ABSTRACT

An entirely new method had previously been perfected (1) for the determination of molecular weight of cellulose acetate in solution. The applicability of the dielectric dispersion method to other cellulosics was the next step in the development of this new procedure.

Ethyl cellulose fractions were refractionated by a fractional precipitation procedure in order to obtain fractions that were homogeneous with respect to chain length. Ethyl acetate and acetone were used in the ratio of three to one (3:1) as solvents, and water acetone in the ratio of ninety-five to five (95:5) was employed as a precipitating agent.

The homogeneous ethyl cellulose fractions were investigated in a number of solvents -- dioxane, benzene, toluene, carbon tetrachloride and n-butyl acetate. This was done in order that the applicability of different solvents could be observed as well as the relation between the viscosity and the critical frequency. The critical frequency is defined as the frequency at which the dispersion is fifty percent completed.

With cellulose acetate in dioxane concentrated solutions (5%) were employed (1). In this investigation only dilute solutions (0.5 grams/100 ml.) were used.

1. Hawkins, M. C., Master of Science Thesis, Virginia Polytechnic Institute, 1956.

Dilute solutions exhibited a sufficient capacitance drop so that a more concentrated solution was not considered necessary. The capacitance drop of ethyl cellulose in dioxane or any of the other solvents investigated was ten times that of cellulose acetate in dioxane.

A concentration range (0.2 - 0.5 grams/100 ml.) was investigated for each fraction in each solvent. Heat treatment of all samples was necessary. This was done to insure complete dissolution of the polymer. If there was incomplete solvation, a scatter of points was observed in each case.

In benzene and toluene a dependence on concentration was noted which can be explained by the absence of hydrogen bonding of solvent with polymer. Dioxane, carbon tetrachloride and n-butyl acetate are all capable of hydrogen bonding. With no hydrogen bonds aggregations are possible and the larger the molecule the lower the critical frequency.

Ethyl cellulose in dioxane, benzene, toluene and carbon tetrachloride was studied using a differential procedure over the frequency range three hundred cycles ($\sim$) to four hundred kilocycles (Kc). The general relationship

$$\log (100[\eta]) = A + B \log (\sqrt{c})$$

held for each solvent system.

Ethyl cellulose in n-butyl acetate was measured by two different methods. The resistance network and the condenser method followed the general relation above and were in agreement.

The results of all five polymer-solvent systems may be seen below:

Dioxane	$\log(100[\eta]) = 2.97 - 0.59 \log(\nu c)$
Carbon Tetrachloride	$\log(100[\eta]) = 3.41 - 0.83 \log(\nu c)$
Benzene	$\log(100[\eta]) = 3.41 - 0.77 \log(\nu c)$
Toluene	$\log(100[\eta]) = 3.23 - 0.65 \log(\nu c)$
n-Butyl Acetate	$\log(100[\eta]) = 3.08 - 0.67 \log(\nu c)$

The usual differential method was not employed with n-butyl acetate because of the higher dielectric constant of this solvent. Higher dielectrics are difficult to measure because of electrode polarization. This polarization is an irreversible reaction taking place at the electrode. The use of glass electrodes was attempted but without success. The condenser method mentioned above or platinization appear to essentially eliminate the difficulty encountered from high dielectric constant solvents.

The degree of substitution exhibited no effect on the critical frequency in the range investigated. This range was small due to the problem of insolubility of the polymer.

The dispersion region occurs in a region of frequencies comparable with that of Debye. It is somewhat broader due to the fact that the Debye curve exhibits only one relaxation time. One would not say that the dispersion was of the resonance absorption type since this is more narrow than the Debye type.

Two dispersion regions were encountered but only one was investigated. The first or low frequency dispersion region was postulated as being related to oscillations about the major axes of an ellipsoid. The second or higher dispersion region was attributed to the minor axes. It was also postulated that the entire polymer chain did not rotate in the a-c field but was a cumulative segmented rotation.

The dispersion region encountered was unlike that of cellulose acetate and many other polymers. The dispersion retion of cellulose acetate extended from several hundred cycles to one hundred kilocycles. Generally the dispersion region of other polymers is encountered at high frequencies (Mc). The ethyl cellulose used in this investigation decreased in dielectric constant from three hundred cycles to four hundred kilocycles as previously mentioned.

The proximity of the dielectric dispersion and a molecular weight distribution was noted. If a sharp fraction of high molecular weight was investigated, a sharp dispersion curve was noted. This exhibited a larger capacitance decrease than one of the same homogeneity but of lower molecular weight. The original material or a blend resulted in a wider dispersion curve.

The method offers the distinct advantage of being extremely reliable with rapidly obtained results.