A study of the reaction between titanium tetrachloride and ethylene glycol : the dielectric constant of tetraethoxytitanium at radio frequencies and low temperatures, the specific conductivity of monochlorotriethoxytitanium
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A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
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Abstract:
Part I A slightly yellow, viscous, polymer-like compound was prepared by reacting ethylene glycol with titanium tetrachloride. A method of purification by precipitation of the compound from a solution in ethyl alcohol with dry diethyl ether was tried.

An analysis of the product of the reaction indicates the presence of 21.98 percent titanium, 16.53 percent ohlorine, 5.34 percent hydrogen, 26.92 percent carbon and 29.23 percent oxygen. The empirical formulae calculated from these data are TiClH12C5O4 based on one Ti atom, or C6H15O5 based on 6 carbon atoms.

The molecular weight determined by the freezing point method is 30. This value is too low to be correct.

The conductivity of a solution of the product of the reaction between ethylene glycol and titanium tetrachloride was measured. A. concentration of four grams of solute in 1000 grams of ethylene glycol exhibited a specific conductivity of 10.9 x 10^-5 reciprocal ohms. Bxe specific conductivity was found to decrease linearly with increasing dilution. The values obtained for the solution of the compound were compared with values for a solution of HCl and a solution of TiCl(OC2H5)3 in glycol and found to be more like TiCl(OC2H5)3.

This compound is decomposed rapidly by heat and slowly with time, with a subsequent loss of chlorine. A second compound which is similar in behavior was made by reacting monochlorotriethoxytitanlum with ethylene glycol. Its properties were not tested since it was also decomposed by heat end with time.

The apparatus used for analysis is described and an attempt made to explain the experimental results.

Part II.

Tetraethoxytitanium has been prepared and purified. The behavior of the dielectric constant of the pure liquid was studied at frequencies ranging from 30 to 100 megacycles, and at temperatures from -54°C to 25°C.

The dielectric constant did not decrease with increasing frequency within the range of measurements, and, therefore does not exhibit anomalous dispersion at those temperatures end frequencies.

Monochlorotriethoxytltenium was prepared end en attempt made to measure the dielectric constant at 1000 cycles end 25°C. It was found, however, that monochlorotriethoxytltenium conducts electricity and the dielectric constant was not measurable with the equipment available.

The specific conductivity of pure monochlorotriethoxytltenium was measured at 25°C and found to be 1.34 x 10^-6 mhos.

A discussion of the difficulties involved in the use of a Q meter is presented.

The apparatus used for measurements is described.

Part I. A STUDY OF THE REACTION BETWEEN TITANIUM TETRACHLORIDE AND ETHYLENE GLYCOL

Part II. THE DIELECTRIC CONSTANT OF TETRAETHOXYTITANIUM AT RADIO FREQUENCIES AND LOW TEMPERATURES. THE SPECIFIC CONDUCTIVITY OF MONOCHLOROTRIETHOXYTITANIUM

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Part I.

I. ABSTRACT

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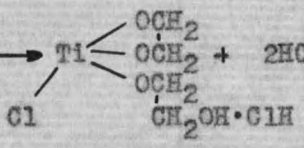
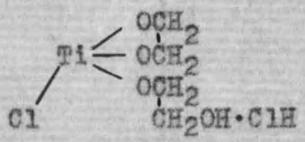
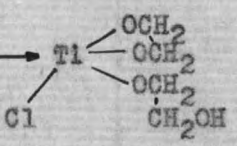
The apparatus used for analysis is described and an attempt made to explain the experimental results.

II. INTRODUCTION

In the course of an investigation by Crowe[5] on the dielectric properties of some esters of titanium tetrachloride, the reaction of this compound with some polyhydroxy alcohols was considered. A viscous, resinous material was produced which on analysis was shown to be nonhomogeneous. Upon consulting the literature, it was found that practically nothing is reported on the chemistry of the reactions of metal halides and polyhydroxy alcohols. Gardiner and Bielouss[10] have proposed the following reactions, although they have established no proof that these are the actual reactions:

1. $TiCl_4 + 2HOCH_2CH_2OH \longrightarrow$  $+ \ 2HCl$

and on further heating:

2.  $+ \ HOCH_2CH_2OH \longrightarrow$  $+ \ H_2O + HOCH_2CH_2Cl$

The water was supposed to react chemically with the chlorine to form a hydroxyester and the freed hydrogen chloride might have converted more glycol to chlorhydrin. The reaction produced a complex mixture of compounds, none of which were isolated or identified by those workers.

It seems probable that the product might be of considerable interest and importance since the nature of the reaction and the properties of the product indicated the possibility of a polymer formation. If polymer formation is possible, these might exhibit some very unusual and valuable properties. Up to the present time no macromolecules containing titanium have been reported.

A more thorough study of the reaction of the method of purification and of the product or products obtained appeared to be of considerable value.

A comparison of the method used by Crowe, and that used by Gardiner and Bielouss for reacting the glycol and titanium tetrachloride indicated that the reaction carried out by Crowe was similar to the first stage of the Gardiner and Bielouss reaction. Elimination of the second stage should make the reaction less complex, and the separation of the titanium glycolate product should not be too difficult. Identification of the compound should follow from a complete analysis and a determination of its molecular weight.

Simplification of the reaction products should result by the use of monochlorotriethoxytitanium and ethylene glycol, or of monochlorotriethoxytitanium and monosodium glycolate. A possible reaction between monochlorotriethoxytitanium and monosodium glycolate is:

$$HOCH_2CH_2ONa + ClTi(OC_2H_5)_3 \longrightarrow HOCH_2CH_2OTi(OC_2H_5)_3 + NaCl$$

whereas, with the monochlorotriethoxytitanium and the ethylene glycol, the reaction may proceed as follows:

$$ClTi(OC_2H_5)_3 + CH_2OHCH_2OH \longrightarrow C_2H_5OH + TiCl(OC_2H_5)_2OCH_2CH_2OH$$

with the ethyl alcohol splitting off rather than the highly negative chlorine atom.

The problems in this first part will be:

(1) to find the reaction which will give the same product or products each time,

(2) to determine a reliable method of isolation and purification of product, and

(3) to determine the structure using analytical, molecular weight, conductivity and other data on the physical properties.

III. REACTION OF TITANIUM TETRACHLORIDE WITH ETHYLENE GLYCOL

The procedure used was essentially that of Crowe, except that the titanium tetrachloride was dissolved in benzene, instead of being added directly to the glycol. In detail, it is as follows. Eight grams of ethylene glycol were added dropwise from a dropping funnel to a solution of five milliliters of titanium tetrachloride dissolved in forty to fifty milliliters of dry benzene in a small three neck flask. The flask was equipped with a mechanical stirrer, a delivery tube, and an outlet tube leading into a solution of sodium hydroxide. Benzene made a good medium in which to carry out the reaction since it reacts with neither of the reactants, and the product was insoluble in it.

The product of the reaction was separated from the benzene by filtration and heated with an oil bath to 125-130°C at reduced pressure for about ten to fifteen hours. The dark brown solid residue was dissolved in dry ethyl alcohol and precipitated as a white solid by addition of anhydrous diethyl ether. After drying in a desiccator at a pressure of 20 mm of mercury for two to three hours a tan colored solid remained. This product was only slightly soluble in ethylene glycol and ethyl alcohol and insoluble in benzene, hexane, cyclohexane, carbon tetrachloride and acetone. It was found that rapid decomposition took place on further heating to 100°C. After continued drying in a desiccator at 20 mm Hg. pressure for fifteen to twenty hours, the residue was analyzed.

IV. ANALYSIS OF COMPOUND

To analyze for titanium, the sample was ignited over a Meker burner, and the titanium calculated on the basis of titanium dioxide. Results of the analysis of the compound for titanium, in this manner, showed that an increase from 22.46% Ti to 30.95% Ti resulted from heating in an oven at 100°C for 2-3 hours. The remainder of the compound was kept in a desiccator over phosphorus pentoxide. The titanium content after two months was 22.63% and after ten months 25.26%.

The analysis for chlorine was carried out in the manner described by Crowe. A sample was weighed into a small round bottom flask fitted with a reflux condenser. A volume of alcohol equal in milliliters to 157 x weight of sample, and a weight of sodium equal in grams to 19.5 x weight of sample, were added to the flask. The mixture was refluxed until the sodium had all reacted. Forty milliliters of water were added and the alcohol distilled off. The solution was acidified with dilute nitric acid and enough silver nitrate was added to precipitate all of the chloride. The solution was then made basic with concentrated ammonium hydroxide, and the titanium hydroxide filtered off. The filtrate was made acid with nitric acid and the silver chloride coagulated by digestion. The silver chloride precipitate was then poured into a gooch crucible, dried, and weighed. The percent chloride was calculated on the basis of silver chloride and was found to be 16.53 and 17.11 in two different samples.

To establish the empirical formula, it was necessary to analyze for carbon and hydrogen. There is no reliable and simple method to analyze for oxygen, so the amount present was obtained by subtracting the total

percentage of Ti, C, H and Cl from 100 percent.

The sample was burned in an atmosphere of oxygen in a combustion tube such as that shown in Figure 1.

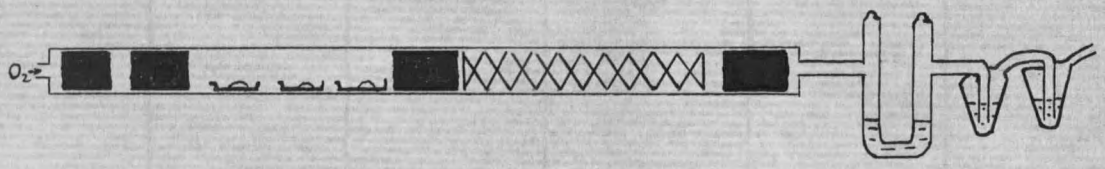


Figure 1

As shown in the figure, the combustion tube contained from left to right, 2 spirals of copper oxide, the porcelain boat containing the sample, 2 boats containing molecular silver to react with the chloride, copper spiral and wire, and finally a reduced copper spiral. The drying tube shown just to the right of the combustion tube contained concentrated sulfuric acid to dissolve the water from the combustion, and the potash bulb contained a 40% solution of potassium hydroxide to react with the carbon dioxide from the combustion. The tube and H_2SO_4, and the bulb and KOH were weighed before and after the experiment. The weights of H_2O and CO_2 were the increase in weight in each case. The percent of hydrogen was calculated on the basis of water. The percent of carbon was calculated on the basis of carbon dioxide.

Results of the analysis gave: 21.98% titanium, 16.53% chlorine, 26.92% carbon, 5.34% hydrogen, and by subtraction, 29.23% oxygen.

The analysis indicated an empirical formula of either $TiClC_5H_{12}O_4$ based on one Ti atom, or $C_6H_{15}O_5TiCl$ based on 6 carbon atoms.

V. MOLECULAR WEIGHT DETERMINATION

In order to find the actual formula of the compound under investigation the molecular weight should be determined. Since the compound is soluble in ethylene glycol and the freezing point of ethylene glycol is $-15^{\circ}C$, this appeared to be a convenient solvent to use for molecular weight determinations by freezing point depression method. The molal freezing point constant for ethylene glycol was obtained using an equation which may be found in any basic physical chemistry book. The equation is:

$$K_f = \frac{M_2 \times \Delta t \times w_1}{1000 \times w_2}$$

where K_f, w_2, w_1, M_2 and Δt are the molal freezing constant, the weight of solute and solvent, the molecular weight of the solute and the freezing point lowering, respectively.

Table I gives the data and results for the molal freezing point constant determination using dioxane as a solute. The molecular weight of the titanium glycolate was calculated, using the same equation, and the molal freezing point constant given in Table I.

TABLE I.

Determination of the Molal Freezing Point Constant of Ethylene Glycol

Trial	Wt. of Dioxane	Wt. of Glycol	Δt	K_f
1	.8678	24.9087	2.44	3.64
2	1.3374	24.5336	2.14	3.50

Table II gives the data and results of the molecular weight determination.

TABLE II.

Determination of the Molecular Weight of Titanium Glycolate

Trial	Wt. of Titanium Glycolate	Wt. of Glycol	Δt	K_f	M
1	.109	32.479	.37	3.64	29.84
2	.133	25.221	.58	3.50	30.03

The value of 30 is too low to be the molecular weight of this compound. This low molecular weight may be a result of any or all of the following: (1) dissociation or reaction of the compound with glycol; (2) association of dioxane and glycol causing an incorrect freezing point constant; (3) impurities in the compound and glycol.

VI. CONDUCTIVITY MEASUREMENTS

Conductivity measurements were made to check dissociation of the compound. Dissociation was indicated since an aqueous or ethylene glycol solution of the compound gave an acid test with litmus. It seemed most probable that chloride ion dissociated from the rest of the molecule, the chloride ion resulting from one or both of the following sources. It might be attached to Ti atom by a partial ionic bond, or it might be bound to a glycol group as molecular HCl.

A comparison has been made between the specific conductivity of a solution of the compound in ethylene glycol, a solution of HCl and a solution of monochlorotriethoxytitanium in the same solvent. The values of concentration and conductivity for hydrochloric acid solution in glycol are much larger than for the compound because the concentration of ions was much greater in the former solutions; whereas, the concentration and conductivity of the monochlorotriethoxytitanium compared favorably in magnitude. The results are recorded in Table III and shown in Figures 2 and 3.

TABLE III.

Concentration of Solutions of Titanium Glycolate, Hydrogen Chloride and Monochlorotriethoxytitanium in Glycol and Corresponding Specific Conductivity in mhos at 25°C

Titanium Glycolate		HCl		Monochlorotriethoxy-titanium	
Conc.[1]	Cond. x 10^5	Conc.[1]	Cond. x 10^5	Conc.[1]	Cond. x 10^5
8.12	21.33	80.41	2210	12.72	35.4
4.06	10.91	40.20	1700	6.14	14.6
2.03	5.98	20.10	1130	3.73	6.54
1.02	3.17	10.05	630	2.60	2.90
.51	1.75	5.02	330	2.22	1.34
.25	.94	2.51	180	1.96	.75
		1.25	100		

A comparison of the results for titanium glycolate and HCl is made in Figure 2, whereas, in Figure 3 the comparison is between the monochlorotriethoxytitanium solution and the titanium glycolate solution.

It should be noted that the specific conductivity of the hydrogen chloride solution and titanium glycolate solution were divided by ten to allow a comparison of the slopes of the curves in Figure 2.

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1 The concentration is in grams of solute per 1000 grams of solvent.

CONCENTRATIONS OF SOLUTIONS OF TITANIUM GLYCOLATE AND HYDROGEN CHLORIDE IN ETHYLENE GLYCOL PLOTTED AGAINST SPECIFIC CONDUCTIVITY AT 25°C

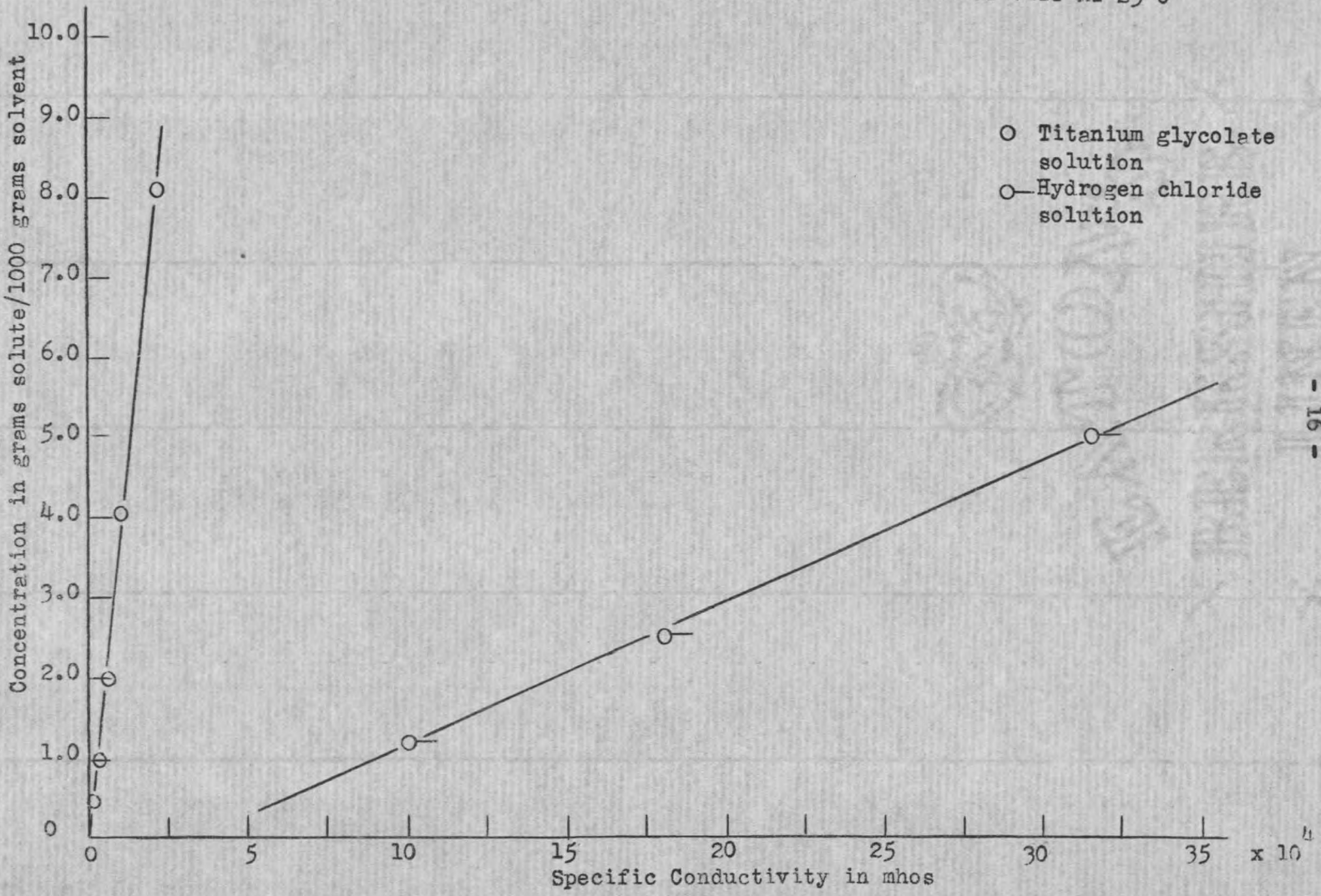
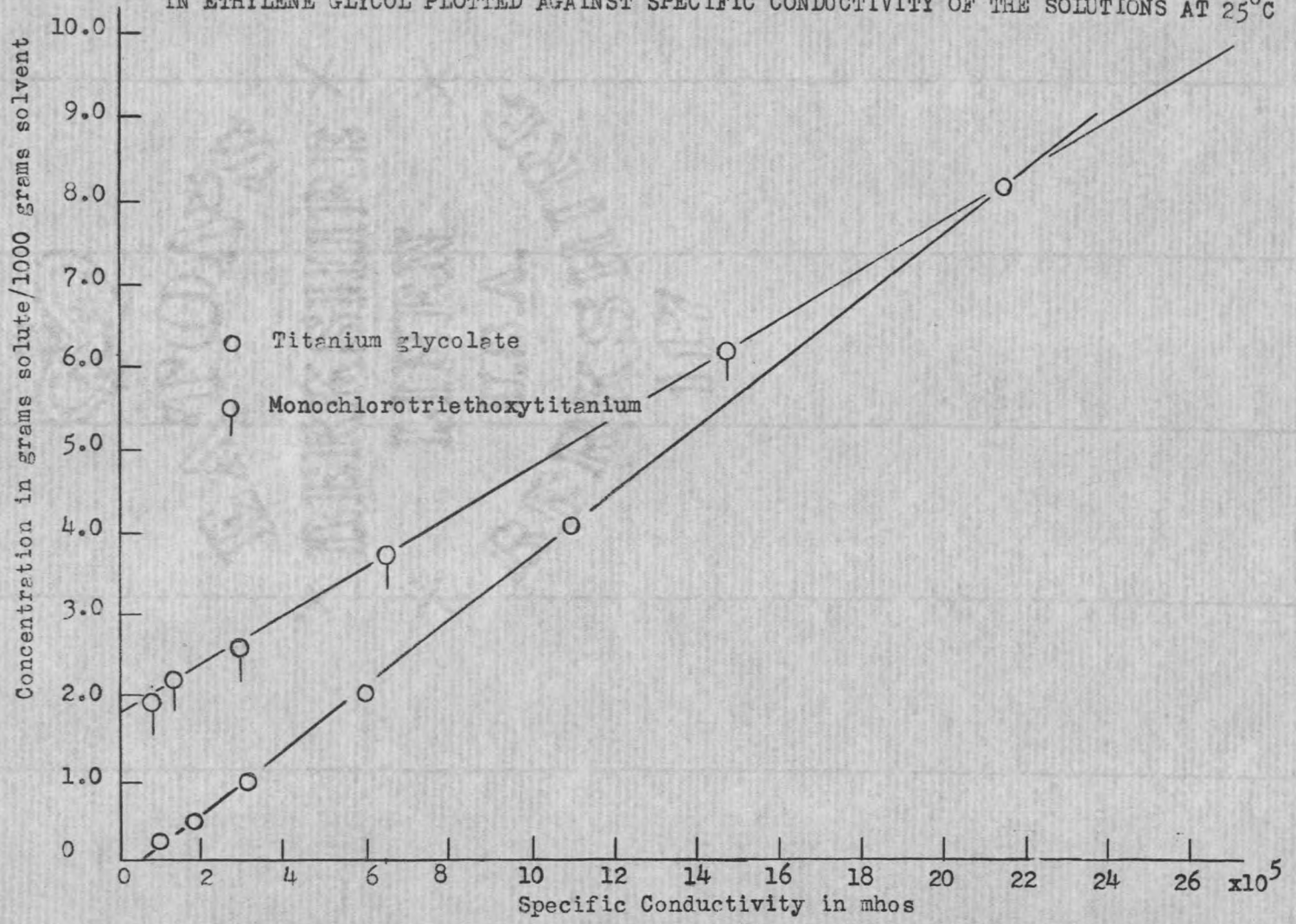


Figure 2

Figure 3

CONCENTRATIONS OF SOLUTIONS OF TITANIUM GLYCOLATE AND MONOCHLOROTRIETHOXYTITANIUM IN ETHYLENE GLYCOL PLOTTED AGAINST SPECIFIC CONDUCTIVITY OF THE SOLUTIONS AT 25°C



VII. OTHER COMPOUNDS MADE

At this point it was decided that because of the complexity, the problem should be attacked from a different angle. If less complex compounds of ethylene glycol and titanium of definitely known structure could be made, and their properties determined, a comparison might be possible between these compounds and the compound just described. It was hoped that compounds made by reacting monochlorotriethoxytitanium with glycol or sodium glycolate would fit that description.

Thus, compounds were prepared as follows: a solution of ten grams of monochlorotriethoxytitanium in glycol was added to four grams of monosodium glycolate in a small round bottom flask equipped with a reflux condenser. No reaction took place at room temperature, so the reactants were heated using a water bath until a white precipitate appeared in the flask. This occurred at a temperature of about 80°C. The reaction flask and contents were heated for about one-half hour and then allowed to cool. The liquid was decanted off and distilled at reduced pressure. It did not contain the desired product. The solid residue in the reaction flask was soluble in water, and ethyl alcohol, and insoluble in benzene, hexane, carbon tetrachloride, acetone and cyclohexane. It tasted like sodium chloride. The problem of separation of the compound from the salt was not solved satisfactorily. The sodium chloride was not entirely insoluble in ethyl alcohol. Water was used finally, but hydrolysis took place in the water solution. This was indicated by the analysis for titanium which was too high for the compound expected.

With the idea in mind of finding a process which produced a product which would be easily purified, the reaction between monochlorotriethoxytitanium and ethylene glycol was tried. There is a possibility that the reaction could be represented by the equation:

$$HOCH_2CH_2OH + ClTi(OC_2H_5)_3 \longrightarrow HOCH_2CH_2OTi(OC_2H_5)_3 + HCl$$

However, with the highly negative chlorine atom the reaction might also proceed as mentioned earlier, i. e.,

$$TiCl(OC_2H_5)_3 + HOCH_2CH_2OH \longrightarrow TiCl(OC_2H_5)_2OCH_2CH_2OH + C_2H_5OH$$

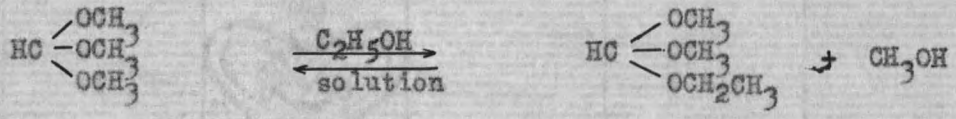
For the reaction 2.85 grams of ethylene glycol were added to 10 grams of monochlorotriethoxytitanium in a small round bottom flask fitted with a reflux condenser. There was no evolution of heat, or other indication of a reaction, so the flask and reactants were heated to about 75°C when the liquid began to reflux. Refluxing was continued for two and one-half hours and the volatile substance distilled off.

The odor and a boiling point indicated the volatile substance was ethyl alcohol, which in turn indicated that the second possibility shown above took place. The residue was a very viscous, clear, colorless liquid which solidified when the pressure was reduced in the flask. The white solid was powdered and it was found to be soluble in ethyl alcohol and ethylene glycol, but not soluble in benzene, hexane, carbon tetrachloride, acetone or cyclohexane. The product was decomposed by heat. Its properties are similar to those of the titanium tetrachloride ethylene glycol product.

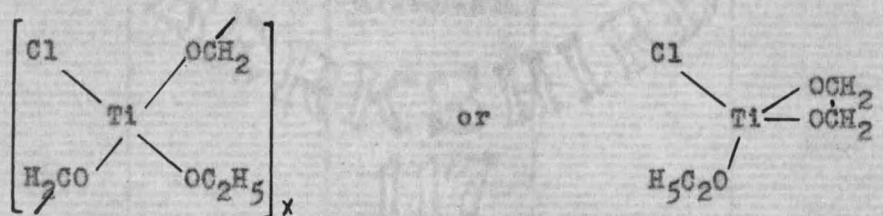
VIII. DISCUSSION OF EXPERIMENTAL RESULTS

Good agreement was obtained between different samples in the analysis of the compound described in Section IV for titanium. This indicated that the product is quite uniform. Repeated attempts at making the compound, produced slightly different results in each case. That would seem to indicate several concurrent reactions or stepwise reactions.

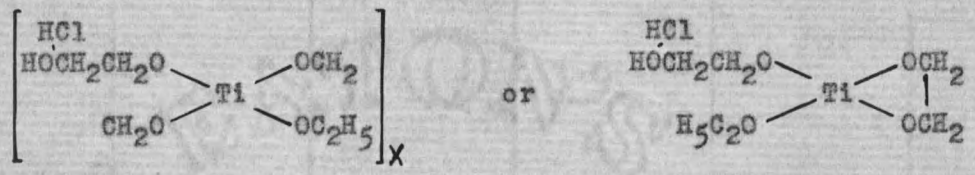
There is a possibility that with the multiple alcohol groups attached to a central atom, the titanium glycolate compound is similar to the acetals. When acetals containing primary alcohol groups are dissolved in other primary alcohols, it is possible that there will be an exchange of those alcohol groups with the solvent which tends toward an equilibrium. As an example:



There is no proof that the above type of reaction takes place with the titanium compound. However it has been demonstrated with the reaction of monochlorotriethoxytitanium with glycol, that one or more ethyl groups on the molecule have been replaced by the glycol. The analytical data and empirical formula for the product of the reaction of titanium tetrachloride with glycol indicates that for one titanium atom, the types of structures shown below are possible.



One is shown here as a unit of a polymer, where the free bonds are actually attached to other carbon atoms of incompletely drawn glycol molecules. The conductivity data gives evidence that these structures are more probable than those possible if the empirical formula is based on six carbon atoms, that is, $C_6H_{15}O_5TiCl$ where the structure may be represented by:



with the chlorine present as molecular hydrogen chloride. Although less probable, this structure could also be possible, since the specific conductivity of both the compound and HCl vary linearly with the concentration.

If this titanium glycolate compound does behave similar to the acetals, there is a possibility that the two structures shown above, and others, were in equilibrium when the ether was added to precipitate the compound. If that was the case, precipitation does not purify the compound. Further work is required to determine this conclusively.

The compound made by reacting monochlorotriethoxytitanium with ethylene glycol behaves in much the same manner and there is a strong probability that it is the same type of complex mixture.

IX. SUMMARY

1. A polymer-like compound was prepared by reacting titanium tetrachloride with ethylene glycol. Precipitation by dry diethyl ether was not proven to be a method of purification.

2. Analysis of the compound gives possible empirical formulae: $TiClC_5H_{12}O_4$ or $C_6H_{15}O_5TiCl$.

3. Conductivity data indicate a possibility of molecular hydrogen chloride or more probably chlorine bound by partial ionic bond to titanium.

4. Difficulty is experienced in determining the correct structural formula because the correct value for the molecular weight was not determined.

5. Methods of preparation and purification of compounds of monochlorotriethoxytitanium were tried. Compounds prepared have properties which are similar to those of the products of the reaction of titanium tetrachloride and glycol.

6. It is suggested that subsequent investigation be made on compounds of a less complex nature like the monochlorotriethoxytitanium - sodium glycolate product with the possibility of correlating the data on those reactions and that of the reaction of titanium tetrachloride and ethylene glycol.

Part II.

X. ABSTRACT

Tetraethoxytitanium has been prepared and purified. The behavior of the dielectric constant of the pure liquid was studied at frequencies ranging from 30 to 100 megacycles, and at temperatures from -54°C to 25°C.

The dielectric constant did not decrease with increasing frequency within the range of measurements, and, therefore does not exhibit anomalous dispersion at those temperatures and frequencies.

Monochlorotriethoxytitanium was prepared and an attempt made to measure the dielectric constant at 1000 cycles and 25°C. It was found, however, that monochlorotriethoxytitanium conducts electricity and the dielectric constant was not measurable with the equipment available.

The specific conductivity of pure monochlorotriethoxytitanium was measured at 25°C and found to be 1.34×10^{-6} mhos.

A discussion of the difficulties involved in the use of a Q meter is presented.

The apparatus used for measurements is described.

XI. INTRODUCTION

Anomalous dispersion, the decrease of the dielectric constant of polar liquids with increasing frequency, has been used for many years to assist in determination of the physical structure of molecules and their size.

Recently, however, it has become increasingly important in electrical engineering laboratories as a means of determining the best use of each dielectric or insulating material. In many cases the dielectric data may be the deciding factor in determining which material is best for dielectric or insulation use. For example, materials which exhibit anomalous dispersion at low frequencies would not be satisfactory for dielectrics in electrical equipment unless the region of anomalous dispersion could be avoided by proper choice of temperature or frequency.

At the present time an extensive study of the dielectric properties of esters of titanium containing organic groups is being carried out in this laboratory. As a part of this study, measurements are being made to determine the effect on the dielectric constant of increasing the frequency.

The compounds available in pure state for such a study are tetraethoxytitanium, monochlorotriethoxytitanium, tetrapropoxytitanium and tetrabutoxytitanium. For the present work, an outline of the Debye theory of anomalous dispersion will be presented, details of the use of a Q meter will be discussed and measurements made on tetraethoxytitanium are presented.

The measurements were made on a Q meter, type 170A which has a frequency range of 30-200 mc. Since the compounds under consideration are

polar, viscous liquids, they should exhibit anomalous dispersion within the frequency range of the Q meter.

XII. LITERATURE SURVEY

Anomalous dispersion was discovered by Drude[9] in 1875. He concluded that the effect which he observed was caused by certain groups in the molecules, for example, OH or NH_2. He based his conclusions on experimental results obtained by measurements on a large number of compounds.

In 1917 Debye[6] presented a theory in which he gave a detailed analysis of anomalous dispersion. This theory correlated the actual structure of molecules with the dispersion discovered by Drude. It has given a nearly complete and simplified picture which has aided in the understanding of the concept of complex dielectric constants and dielectric loss.

Oncley and Williams[16] have tested the Debye theory using dilute non-aqueous solutions and found that although the theory was basically sound, corrections were necessary to correlate the experimental with the calculated results. Kirkwood and Fuoss[14], on the other hand, proposed a theory for anomalous dispersion in polymers which has been verified by Smyth[18]. Malsch[15] has made corrections for associated liquids and Debye[7] has made a correction for pure liquids based on a quasi-crystalline concept. Measurements of anomalous dispersion and dielectric loss in industrial materials have been made by Yager and Baker[19] and Smyth[18] and others using the Kirkwood and Fuoss equations, or an adaptation of the Debye equation.

XIII. THEORETICAL DISCUSSION

The theory of anomalous dispersion has been thoroughly treated by Debye[6,7] and others so that a detailed derivation will not be given here. However, a few points of interest concerning pure liquids, the type presently under investigation and a general outline of the theory, will be considered.

According to Debye, an orientation polarization results when an electric field is applied to any material containing dipoles that are able to orient. This polarization is in addition to the polarization due to the displacement of electrons or atoms. The existence of this orientation polarization is due to the tendency of the dipoles to align themselves with the field, and its formation is opposed by the thermal motion of the molecules, or internal friction caused by molecular bombardments, which tends to keep the dipoles randomly oriented. This orientation polarization is therefore dependent on the temperature in two ways. First, a lower temperature will allow an increase in the polarization because the thermal motion is less. Second, a lower temperature will result in a decrease in the polarization due to increased internal friction or viscosity because of the stronger forces of attraction between the molecules. These two effects will vary according to the nature of the liquid under investigation. At room temperature, however, the orientation polarization will, in general, be greater than at higher temperatures because the thermal motion of the molecules interferes less with orientation.

The orientation polarization also depends on the frequency. This is because a finite time is necessary for the molecules to become oriented, and they contribute to the polarization only when the frequency is low enough to permit orientation before the field is reversed.

An outline of Debye's theory of anomalous dispersion in polar liquids is presented below.

First consider a spherical surface drawn in a liquid, and take the center of this sphere as the origin of a system of polar coordinates. Under the influence of an alternating electric field the distribution function of the electric moments depends upon the polar angle ϑ, between the field and the dipole, and upon time. The number of molecules which have their moments in the direction of a solid angle $d\Omega$ at a given time will be $fd\Omega$, where f is the distribution function. A time interval δt is chosen such that all moments in the solid angle at time $t = 0$ have moved out of the solid angle, yet have not moved more than a few degrees.

The number of molecules whose moments have entered $d\Omega$ in time interval δt is given by the equation:

$$\delta t \frac{\partial f}{\partial t} d\Omega = \Delta_1 + \Delta_2 \qquad (1)$$

where Δ_1 is the contribution due to rotations produced by the impressed field, and Δ_2 is the contribution due to rotations produced by Brownian movement.

Consider the contribution due to Brownian movement first. Visualize a second solid angle $d\Omega'$ whose axis makes an angle θ with the axis of $d\Omega$. The number of molecules whose moments are in $d\Omega'$ at time $t = 0$ are

$fd\Omega'$. See Figure 4.

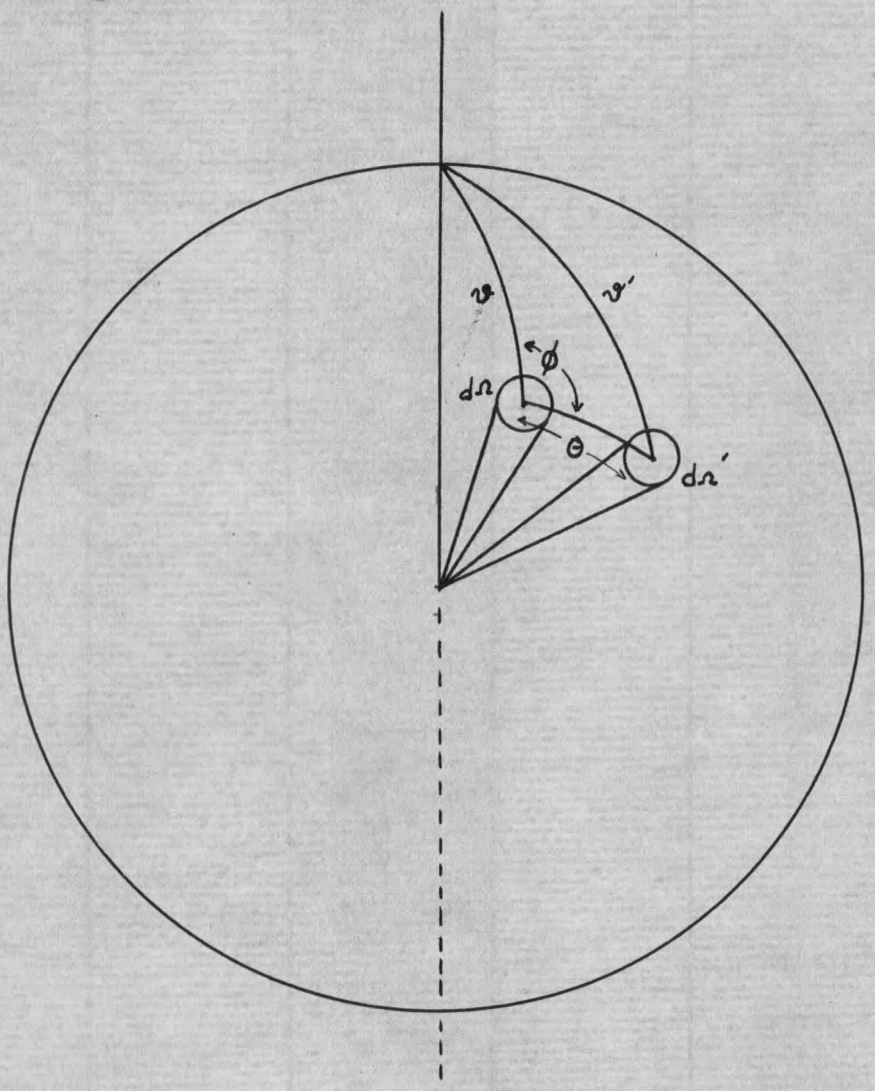


Figure 4

Now suppose a certain probability function W exists, such that $Wd\Omega$ gives the probability that a molecule whose moment is in $d\Omega'$ at time $t = 0$ will be in $d\Omega$ at $t = \delta t$. The total number of molecules whose moments have entered

$d\Omega$ due to Brownian movement is given by the equation:

$$\Delta_2 = -f d\Omega + \int f' d\Omega' W d\Omega \qquad (2)$$

The integration is carried out over the surface of the sphere of unit radius while $d\Omega$ is constant. Factoring $d\Omega$ out of the expression it is seen that:

$$\Delta_2 = d\Omega \left[\int f' d\Omega' W - f \right] \qquad (2)'$$

The function f' is expanded about its value at $d\Omega$

$$f' = f - \frac{\partial f}{\partial \vartheta}(\vartheta' - \vartheta) - \frac{\partial^2 f}{\partial \vartheta^2} \frac{(\vartheta' - \vartheta)^2}{2} - \ldots \qquad (3)$$

Since the moments can move only a few degrees in time δt, the angle θ is small, and $\vartheta' - \vartheta$ is therefore also small so that the fourth and higher terms of the expansion may be neglected. Letting $\vartheta' - \vartheta = \epsilon$ we can express the integral in equation $(2)'$ as

$$\int f' W d\Omega' = f \int W d\Omega' + \frac{\partial f}{\partial \vartheta} \int \epsilon W d\Omega' - \tfrac{1}{2} \frac{\partial^2 f}{\partial \vartheta^2} \int \epsilon^2 W d\Omega'. \qquad (4)$$

The first integral on the right side of the equation is equal to unity, the second integral represents the mean value, $\bar{\epsilon}$, of ϵ corresponding to the time interval δt, and the third integral represents the mean square value, $\overline{\epsilon^2}$, of ϵ. These integrals are evaluated using spherical trigonometry. The cosine theorm of spherical trigonometry is expanded using the sine and cosine series from general trigonometry. For small values of θ it is written as :

$$\cos \vartheta' = \cos \vartheta + \theta \sin \vartheta \cos \phi - \frac{\theta^2}{2} \cos \vartheta + \ldots$$

Expansion of the value $\vartheta' = \vartheta + \epsilon$ for $\cos \vartheta'$ using the Taylors series gives:

$$\cos \vartheta' = \cos \vartheta - \epsilon \sin \vartheta - \frac{\epsilon^2}{2} \cos \vartheta + \ldots$$

ϵ is now expanded in powers of θ.

$$\epsilon = \alpha\theta + \beta\theta^2 + \ldots$$

where the coefficients involve functions of ϑ and ϕ implicitly. The explicit form of the coefficients of this expansion may be obtained by substituting in the last written expansion for $\cos\vartheta'$ and then by comparing the two expansions for $\cos\vartheta'$. The expression obtained is averaged over all directions and gives =

$$\bar{\epsilon} = \frac{\overline{\theta^2}}{4}\,\frac{\cos\vartheta}{\sin\vartheta}$$

where $\overline{\theta^2}$ is the mean square value of θ and is

$$\overline{\theta^2} = \int_0^{\pi}\int_0^{2\pi} \theta^2 W \sin\theta \, d\theta \, d\phi$$

$\overline{\epsilon^2}$ is evaluated in a similar manner giving

$$\overline{\epsilon^2} = \int \epsilon^2 W d\Omega' = \frac{\overline{\theta^2}}{2}$$

and finally

$$\int f' d\Omega' = f + \frac{\partial f}{\partial\vartheta}\,\frac{\overline{\theta^2}}{4}\,\frac{\cos\vartheta}{\sin\vartheta} + \frac{\overline{\theta^2}}{4}\cdot\frac{\partial^2 f}{\partial\vartheta^2}$$

giving for Δ_2

$$\Delta_2 = d\Omega\,\frac{\overline{\theta^2}}{4}\left[\frac{\cos\vartheta}{\sin\vartheta}\,\frac{\partial f}{\partial\vartheta} + \frac{\partial^2 f}{\partial\vartheta^2}\right] \qquad (5)$$

In this equation we see that if f is independent of ϑ the Brownian movement can have no effect on the distribution function.

For the determination of the Δ_1, the number of molecules whose moments have entered $d\Omega$ in time δt due to action of the impressed field, we take into account the torque on a given molecule tending to turn it in the direction of the field. The torque may be represented by the equation

$$M = -\mu F \sin\vartheta$$

where μ is the electric moment and F is the force of the field and the negative sign takes account of the fact that the torque acts opposite to the direction of increasing ϑ.

A torque due to an inner frictional force resulting from molecular impacts and proportional to the angular velocity, would just balance the constantly impressed torque. We express this by the equation

$$M = \rho \frac{d\vartheta}{dt}$$

where ρ is a constant measuring the inner friction of the liquid.

If applied to the case where the torque is not constant it is implied that the acceleration effect is negligible. In an interval δt the molecule will turn through the angle

$$\delta\vartheta = \delta t \frac{M}{\rho}$$

Now determine the number of molecules which enter a solid angle consisting of a strip extending between ϑ and $\vartheta + d\vartheta$ around the sphere. The number of molecules whose moments pass through the circle $\vartheta = \vartheta$ in interval δt is

$$2\pi f \sin\vartheta \delta\vartheta = 2\pi f \frac{M}{\rho} \delta t \sin\vartheta$$

and through $\vartheta - d\vartheta$ in the same δt is

$$2\pi f \frac{M}{\rho} \delta t \sin\vartheta + \frac{\partial}{\partial\vartheta} (2\pi f \frac{M}{\rho} \delta t \sin\vartheta) d\vartheta$$

Subtracting the second expression from the first

$$\Delta_1 = \frac{-\partial}{\partial\vartheta} (2\pi f \frac{M}{\rho} \delta t \sin\vartheta) d\vartheta \qquad (6)$$

Substituting expressions derived for Δ_1 and Δ_2 in equation (1), and remembering

$$d\Omega = 2\pi \sin\vartheta d\vartheta$$

one obtains

$$\frac{\partial f}{\partial t} = \frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta}\left[\sin\vartheta\left(\frac{\bar{\theta}^2}{4\delta t} \frac{\partial f}{\partial\vartheta} - \frac{M}{\rho} f\right)\right] \qquad (7)$$

For a special case when the field F is constant, then the Maxwell Boltzmann expression

$$f = Ae^{-u/kT} = Ae^{F\cos\vartheta/kT}$$

is a solution of the differential equation if $\frac{\partial f}{\partial t} = 0$. u is the potential energy of the molecules, μ is the electric moment, F is the field intensity, k is the Boltzmann constant, T is the absolute temperature and e is the exponential.

Since the torque

$$M = -\mu F \sin\vartheta = -\frac{\partial u}{\partial\vartheta}$$

it may be seen that the Maxwell Boltzmann expression is a solution of the differential equation for the condition $\frac{\partial f}{\partial t} = 0$ providing

$$\frac{\bar{\theta}^2}{4\delta t} = \frac{kT}{\rho}$$

This equation expresses the relation which exists between the magnitude of the Brownian force of this angle and the temperature and friction constant of the molecules. Substituting

$$\frac{kT}{\rho} \quad \text{for} \quad \frac{\bar{\theta}^2}{4\delta t} \qquad (8)$$

from (8) in (7) one obtains the final differential equation necessary to determine the distribution function f as a function of t and the angle ϑ

$$\rho \frac{\partial f}{\partial t} = \frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta}\left[\sin\vartheta\,(kT \frac{\partial f}{\partial\vartheta} - Mf)\right] \qquad (9)$$

For a polar liquid under the influence of high frequency, the internal force may be expressed by the real part of $F = F_o e^{iwt}$, so that

the torque on a molecule is

$$M = -\mu F_o e^{iwt} \sin\vartheta$$

where F is the intensity of the field, w is $2\pi f$ where f is the frequency. The distribution function must be a solution of (9), which can be written

$$2\tau \frac{\partial f}{\partial t} = \frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta}\left[\sin\vartheta\left(\frac{\partial f}{\partial\vartheta} - \frac{fM}{kT}\right)\right] \qquad (10)$$

where τ is the time of relaxation for the liquid and is equal to $\gamma/2kT$. A solution is $f = A\left[1 + \frac{B\mu F_o e^{iwt}}{kT} \cos\vartheta \right]$ where B is an arbitrary constant, can be shown by substituting this solution in equation (9) providing $B = \frac{1}{1 - iw\tau}$

Thus

$$f = A\left[1 - \frac{1}{1 - iw\tau} \frac{\mu F_o}{kT} \cos\vartheta\right] \qquad (11)$$

For large values of $w\tau$ the function becomes constant. The transition occurs where $w\tau$ is nearly unity. The mean moment of the molecules is also complex and is given by the equation:

$$\bar{m} = \frac{\mu^2}{3kT} \cdot \frac{F}{1 + iw\tau} = \frac{\mu^2}{3kT} \frac{F_o e^{iwt}}{1 + iw\tau} \qquad (12)$$

which will be treated in more detail later.

The meaning of the complex moment is that there is a difference in phase between the moment and the internal force. If the phase angle is φ, the above equation may be written:

$$\bar{m} = \frac{\mu^2}{3kT} \frac{F_o}{\sqrt{1 + w^2\tau^2}} e^{i(wt - \varphi)} \qquad (13)$$

where $\tan\varphi = w\tau$

It is well known that the difference in phase between field intensity and polarization is always accompanied by energy adsorption. As a result of a finite relaxation time we encounter absorption as well as dispersion. This phenomenon will be considered later.

The general formula for the polarizability was shown by Debye[6] to be:

$$\alpha = \alpha_0 + \frac{\mu^2}{3kT}$$

where α_0 is the polarizability due to distortion and $\frac{\mu^2}{3kT}$ is that due to orientation. The mean moment was shown to be

$$\vec{m} = \left(\alpha_0 + \frac{\mu^2}{3kT}\right) F \qquad (14)$$

This equation may be obtained by adding the mean moment due to distortion to that calculated for the expression for the mean moment due to orientation

$$\bar{m}_0 = \frac{\int_{Ae} F\cos\vartheta/kT \; \mu\cos\vartheta \, d\Omega}{\int_{Ae} F\cos\vartheta/kT \; d\Omega}$$

where $Ae^{F\cos\vartheta/kT}$ is the number of molecules confined to the solid angle $d\Omega$ according to Boltzmann's law, and $\mu\cos\vartheta$ is the component of the moment of a molecule in the direction of the field. The expression is integrated over all directions and $\bar{m}_0$ is found to be $\frac{\mu^2 F}{3kT}$. For high frequencies the moment of a polar liquid will be complex and a function of the frequency as shown in equation (12). The mean moment due to orientation then is

$$\bar{m}_{(w)} = \frac{\mu^2}{3kT} \cdot \frac{F}{1 - iw\tau} \qquad (15)$$

Substituting that value of the polarizability due to orientation

$$\alpha'_{(w)} = \frac{\mu^2}{3kT} \cdot \frac{F}{1 + iw\tau}$$

with equation (14), the total mean moment is shown to be

$$\bar{m}_{(w)} = \left(\alpha_0 + \frac{\mu^2}{3kT} \cdot \frac{1}{1 + iw\tau}\right) F \qquad (16)$$

and the total polarizability $\alpha_{(w)} = \alpha_0 + \frac{\mu^2}{3kT} \cdot \frac{1}{1 + iw\tau}$

Substituting this in the equation for molar polarization as derived by Mossotti where N is Avogadro's number, α the polarizability, ϵ the dielectric constant, M the molecular weight and d the density of the substance.

$$P = \frac{4}{3}\pi N\alpha = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$$

one obtains:

$$P_{(w)} = \frac{4}{3}\pi N\left(\alpha_0 + \frac{\mu^2}{3kT} \cdot \frac{1}{1 + iw\tau}\right) = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} \qquad (17)$$

which, it will be noted is complex and a function of the frequency. $P_{(w)}$ the molar polarization is related to the dielectric constant by the Clausius Mossotti equation and is the sum of two terms. The first is part of the polarization due to electronic and atomic motions within the molecule also called distortion. This polarization is present in all dielectrics whether polar or not. The second term

$$\frac{4\pi N}{3} \times \frac{\mu^2}{3kT} \times \frac{1}{1 + iw\tau}$$

is the part due to orientation of dipoles. μ is the electric moment of the molecule, k is Boltzmann's constant, T is the absolute temperature and τ is the relaxation time for the molecules.

Assuming Mossotti's hypothesis to hold, we will consider the connection between dispersion and absorption. If the equation

$$P_{(w)} = \frac{\epsilon - 1}{\epsilon - 2} \cdot \frac{M}{d} = \frac{4\pi N}{3}\left(\alpha_0 + \frac{\mu^2}{3kT} \cdot \frac{1}{1 + iw\tau}\right) \qquad (18)$$

is solved for ϵ one finds:

$$\epsilon = \frac{1 + 2\,\frac{d}{M}\,P_{(w)}}{1 - \frac{d}{M}\,P_{(w)}} \qquad (19)$$

Instead of characterizing the liquid by α_0 and $\frac{\mu^2}{3kT}$, two dielectric constants ϵ_0 and ϵ_1 are used. They are defined by setting limits on equation (18) when $w = \infty$ and $w = 0$.

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} \cdot \frac{M}{d} = \frac{4}{3}\pi N \alpha_0 \qquad (w = \infty)$$

$$\frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{M}{d} = \frac{4}{3}\pi N\left(\alpha_0 + \frac{\mu^2}{3kT}\right) \qquad (w = 0) \tag{20}$$

ϵ_0 the optical dielectric constant, will denote the value for ϵ at high frequency, and is equal to n^2, where n is the index of refraction, and ϵ_1 will be the statistical dielectric constant at $w = 0$. Using these definitions we define $P_{(w)}$

$$P_{(w)} = \frac{M}{d}\left[\frac{\epsilon_0 - 1}{\epsilon_0 + 2} + \frac{1}{1 + iw\tau}\left(\frac{\epsilon_1 - 1}{\epsilon_1 + 2} - \frac{\epsilon_0 - 1}{\epsilon_0 + 2}\right)\right]$$

The dielectric constant as a function of w is then expressed:

$$\epsilon = \frac{\frac{\epsilon_1}{\epsilon_1 + 2} + iw\tau\,\frac{\epsilon_0}{\epsilon_0 + 2}}{\frac{1}{\epsilon_1 + 2} + iw\tau\,\frac{1}{\epsilon_0 + 2}} \tag{21}$$

But, according to the formal theory of the propagation of light for a complex dielectric constant

$$\epsilon = r^2 (1 - i\kappa)^2 \tag{22}$$

r and κ are real quantities being the ordinary index of refraction, and the absorption index, respectively. The variable

$$x = \frac{\epsilon_1 + 2}{\epsilon_0 + 2}\, w\tau$$

is introduced to present r as a function of the frequency. The equation (5) may be shown to be equivalent to

$$r^2 = \frac{1}{2}\left[\frac{\sqrt{\epsilon_1^2 + \epsilon_0^2 x^2}}{1 + x^2} + \frac{\epsilon_1 + \epsilon_0 x^2}{1 + x^2} \right] \qquad (23)$$

in the interval $x = 0 \cdots x = \infty$, the square of the refractive index range from $r^2 = \epsilon_1$ to $r^2 = \epsilon_0$.

The absorption index K has a maximum value for frequency w given by the formula

$$w\tau = \frac{\epsilon_0 + 2}{\epsilon_1 + 2} \sqrt{\frac{\epsilon_1}{\epsilon_0}} \qquad (24)$$

the maximum value is $K_{max} =$

$$\frac{\sqrt{\epsilon_1} - \sqrt{\epsilon_0}}{\sqrt{\epsilon_1} + \sqrt{\epsilon_0}} \qquad (25)$$

At the corresponding frequency

$$r^2 = \frac{1}{2} \frac{\sqrt{\epsilon_0 \epsilon_1}}{\epsilon_0 + \epsilon_1} \left(\sqrt{\epsilon_0} + \sqrt{\epsilon_1} \right)^2 \qquad (26)$$

For actual experiments on adsorption, the results are often given in terms of a phase angle Φ. If the potential difference between the plates of the condenser is Ve^{iwt} where V is voltage or potential difference, the dielectric constant ϵ is complex and is shown as

$$\epsilon = \epsilon' - i\epsilon'',$$

ϵ'' is called the dielectric loss or dissipative factor,

The charge on one of the plates (omitting constants) will be:

$$Q = (\epsilon' - i\epsilon'') Ve^{iwt}$$

the phase angle can be defined by the equation:

$$\text{Tan } \Phi = \frac{\epsilon''}{\epsilon'}$$

Going back to equations (5) and (6) it can be seen that:

$$\epsilon' = \epsilon_o + \frac{\epsilon_1 - \epsilon_o}{1 + x^2} = \epsilon_o + \frac{\epsilon_1 - \epsilon_o}{1 + \left(\frac{\epsilon_1 + 2}{\epsilon_o + 2}\right)^2 w^2\tau^2} \qquad (27)$$

$$\epsilon'' = \frac{\epsilon_1 - \epsilon_o}{1 + x^2} \; x = \frac{(\epsilon_1 - \epsilon_o)\left(\frac{\epsilon_1 + 2}{\epsilon_o - 2}\right) w\tau}{1 + \left(\frac{\epsilon_1 + 2}{\epsilon_o + 2}\right)^2 w^2\tau^2} \qquad (28)$$

Bolton[2] has shown that by using Onsager's equation:

$$\frac{(\epsilon_1 - \epsilon_o)(2\epsilon_1 + \epsilon_o)}{\epsilon_1 (\epsilon_o + 2)^2} = \frac{4}{9}\pi N \frac{\mu_o^2}{kT} \qquad (29)$$

a circle, the locus of points of (ϵ', ϵ'') with a parameter $w\tau$ is nearly identical with a circle given by Debye with the locus of points of (ϵ', ϵ'') and a parameter X. Therefore $X = w\tau$ and the equations for the real and imaginary part of the dielectric constant are:

$$\epsilon' = \epsilon_o + \frac{\epsilon_1 - \epsilon_o}{1 + w^2\tau^2} \qquad (30)$$

$$\epsilon'' = \frac{(\epsilon_1 - \epsilon_o) w\tau}{1 + w^2\tau^2} \qquad (31)$$

The dielectric loss factor varies with the frequency as shown in equation 31. At both high where $w \gg \frac{1}{\tau}$ and low frequencies where $w \ll \frac{1}{\tau}$ the loss factor approaches zero. It has a maximum value when $w = \frac{1}{\tau}$ where $\epsilon'' = \frac{1}{2}(\epsilon_1 - \epsilon_o)$ This equation predicts how the dielectric loss will depend on the statistical and optical dielectric constants.

For pure liquids, Debye has shown that the molecules are influenced by two kinds of forces. First, the molecules are exposed to the usual couple due to the external field and second, there exists a potential energy which acts to hold the molecules in their instantaneous positions

fixed by their surroundings. Debye assumes that for potential energy, the simple approximation $u = -E \cos\theta$ where θ is the angle between the axis of the permanent electric moment and the instantaneous axis fixed by the surroundings. He has derived equations for the average moment in the direction of the field strength F where:

$$\bar{m}_f = \frac{\mu^2 F e^{iwt}/3kT}{1 + \frac{iwe}{2kT}} \qquad (B = 0)$$

and

$$\bar{m}_f = \frac{\mu^2 F e^{iwt}/\frac{3E}{2}}{1 + \frac{i\rho w}{2\frac{E}{2}}} \qquad (B \gg 1)$$

where $B = \frac{E}{kT}$, $\rho = f = 8\pi\eta a^3$ the internal friction, where η is the inner friction constant for the liquid, and E is the binding energy. So that for a pure liquid the polarization becomes

$$P(w) = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4}{3}\pi N\left(\alpha_o + \frac{\mu^2 F e^{iwt}/\frac{3E}{2}}{1 + \frac{i\rho w}{2\frac{E}{2}}}\right)$$

It is seen that the transition from the case of that of free dipoles to strongly bound dipoles can be performed by replacing the thermal energy kT by the much larger energy $\frac{E}{2}$ where E is the binding energy. It follows then from the formula for dielectric losses and for dispersion effect that we have at the same time a diminishing of the dipole action to be observed both in the dielectric constant itself and in the losses. The binding energy is acting just as if the constant $\rho = 8\pi\eta a^3$ had been diminished and this can be interpreted by saying either that the viscosity η is less than normal or that the molecular radius is smaller than would be expected.

The dipole moment of the pure tetraethoxytitanium can be expected to be less for the pure liquid than that for dilute solutions. Since the orientation moment of tetraethoxytitanium is caused by rotation of the ethyl group about the carbon oxygen bond, it may be that no definite time of relaxation can be expected. For monochlorotriethoxytitanium, on the other hand, with the Ti-Cl bond a rigid one, a greater dielectric constant, electric moment, dielectric loss, than that for tetraethoxytitanium might be expected.

XIV. PREPARATION OF COMPOUNDS

Tetraethoxytitanium

This compound was prepared according to Bischoff and Adkins[1] by the reaction $TiCl_4 + 4NaOC_2H_5 \longrightarrow Ti(OC_2H_5)_4 + 4NaCl$. The procedure is described by Crowe. If the pure liquid is allowed to come in contact with moisture, it hydrolyzes forming the hydrated oxide and ethyl alcohol. Prolonged exposure to air, even dry air, produces a change in color from colorless to yellow, to orange and finally red. Distillation at reduced pressure, using decolorizing charcoal in the Claisson flask, removes the color.

Monochlorotriethoxytitanium ($TiCl(OC_2H_5)_3$)

This compound was prepared according to Jennings, Wardlaw and Way[12] by the reaction:

$$Ti(OC_2H_5)_4 + CH_3COCl \longrightarrow TiCl(OC_2H_5)_3 + CH_3COOC_2H_5$$

and is also described by Crowe. An analysis gave 21.86 and 21.87% titanium. The theoretical value is 21.92%. The chlorine analysis indicates 16.37, whereas the theoretical value is 16.23%.

XV. MEASUREMENT OF THE DIELECTRIC CONSTANT OF TETRAETHOXYTITANIUM AT VARYING TEMPERATURES AND FREQUENCIES

The dielectric constant of pure $Ti(OC_2H_4)_4$ has been determined at frequencies varying by intervals of 5 megacycles, from 30 to 100 megacycles and temperatures ranging from 25°C to -54°C. A discussion of the difficulties encountered is given and mathematical equations used in calculations discussed.

(a) Apparatus Used for Measurements

The instrument used for measurements of the dielectric constants was a Q meter type 170A manufactured by the Boonton Radio Corporation. A schematic diagram of the circuit[3] is shown in Figure 5. The circuit constants are listed by number in Table IV below.

Table IV.

Circuit Constants for Q Meter Type 170-A

Resistors	Condensers	Tubes
1. 24000 Ω ½w	1. 20 μμf zero temp.	1. Type 9002
2. 1000 Ω ½w	2. 240 μμf mica	2. Type OS-VM-955
3. 1000 Ω ½w	5. 240 μμf mica	3. Type Q-VM-955
4. 1000 Ω ½w	6. 240 μμf mica	4. Type VR-105-30
5. 3 meg. Ω 1/3w	7. 510 μμf mica	5. Type VR-105-30
6. 7500 Ω Pot 3w	8. 510 μμf mica	6. Type 5 W 4
7. 200 Ω Pot 3w	9. 240 μμf mica	7. Mazda 47-(6V)
8. 1000 Ω Pot 3w	10. Q Tuning, Air	
9. 20000 Ω Dual Pot 8w	11. 4 μf.)	
10. 200 Ω Pot 3w	12. 4 μf.) Electrolytic	
11. 15000 Ω ½w	13. 4 μf.)	Inductors
12. 24000 Ω ½w	14. Osc. Tuning, Air	
13. 24000 Ω ½w		1. Osc. Grid
14. 40000 Ω 10w	C_x. Test Condenser	2. Osc. Coupling
15. 1200 Ω ½w		3. Osc. Plate
16. 25000 Ω 10w		4. Pwr. Choke
17. 3500 Ω 20w		5. Pwr. Transf.
18. 0.8 Ω 2w		
19. 20000 Ω Pot 3w		
20. 51 Ω 1/3w		L_x. Test Coil

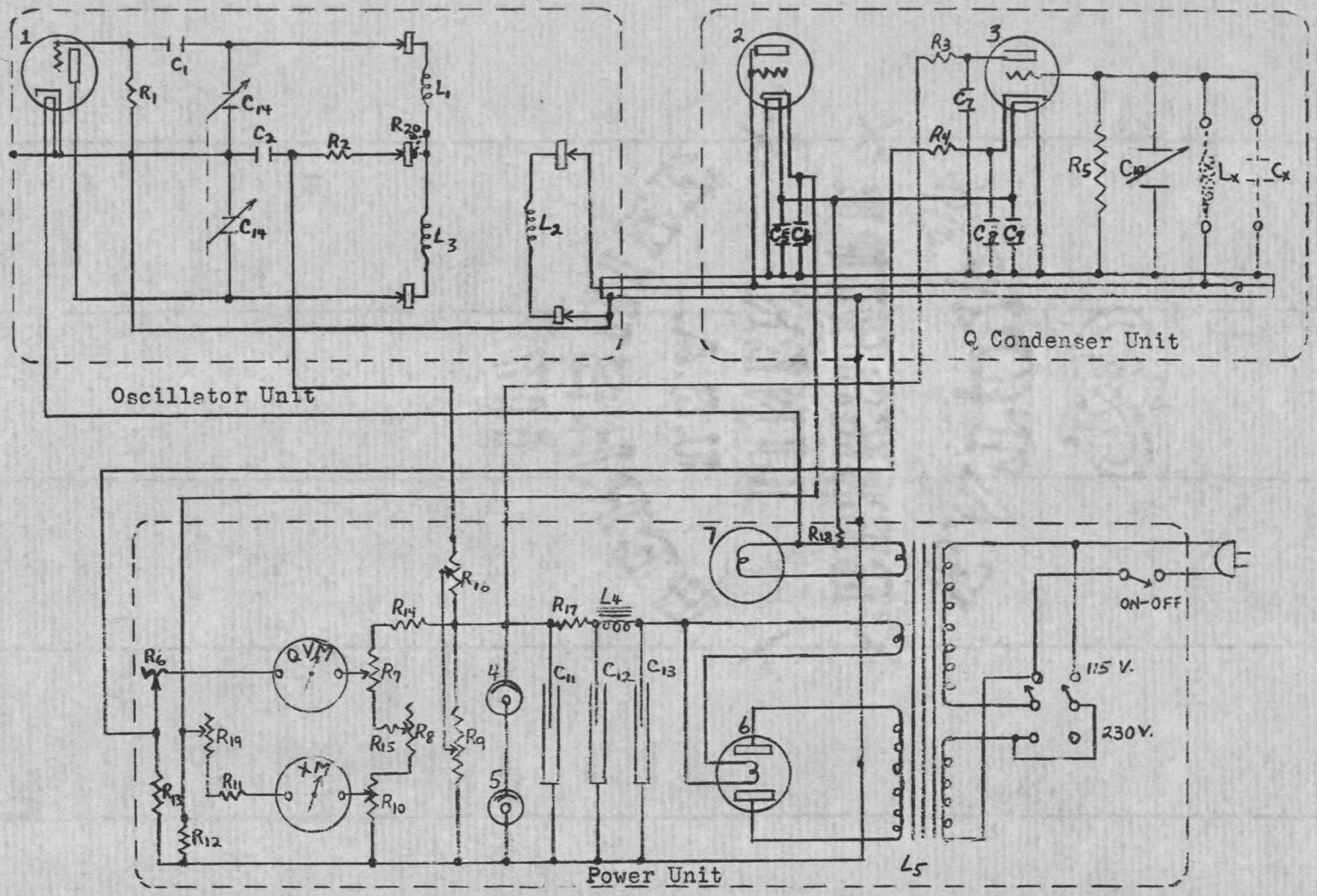


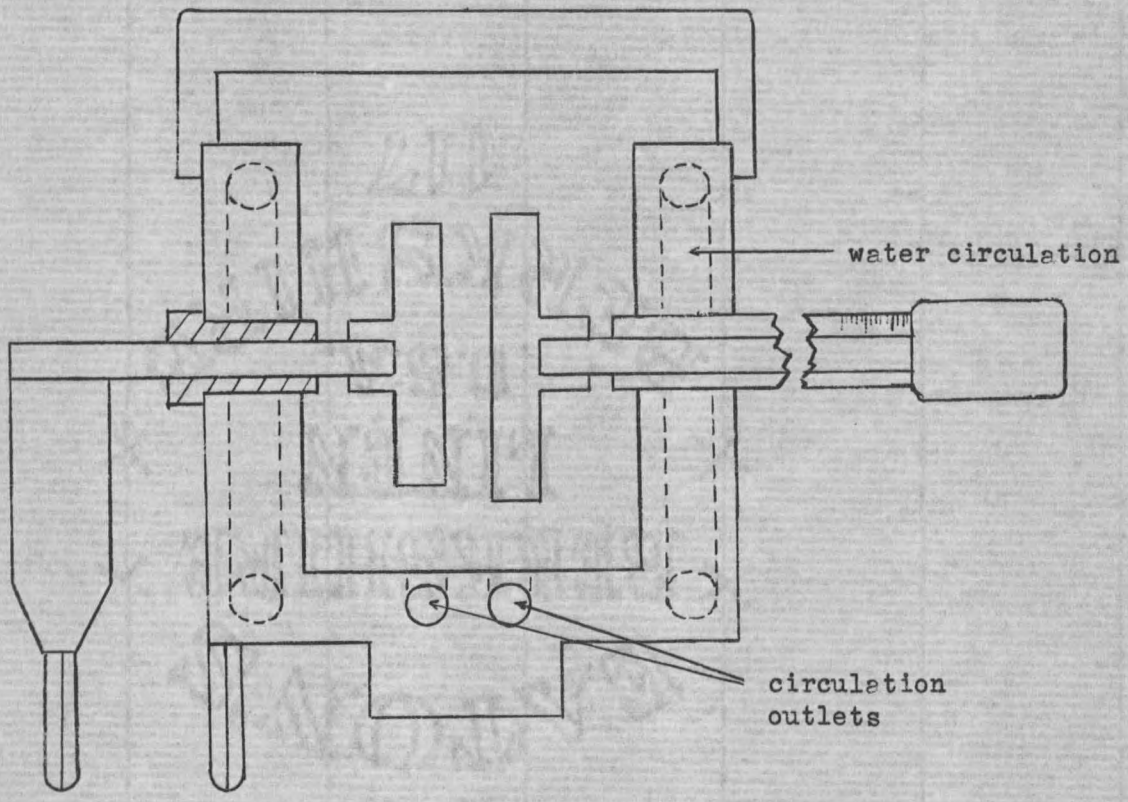
Figure 5

SCHEMATIC DRAWING OF Q METER CIRCUIT

The Q voltmeter is calibrated directly in Q from 80 to 300. The "Multiply Q by" meter is calibrated from x 1 to x 4, hence the total range is from 80 to 1200. The accuracy of the direct reading measurements of circuit Q (for Q voltmeter readings between 100 and 300) is approximately plus or minus 10% up to 100 mc. and decreases with increasing frequency. The range of the capacitance of the Q condenser is 11-60 $\mu\mu$f calibrated in units of $\mu\mu$f. Accuracy is generally $\pm$ 2% on capacitance readings. The power supply is a self contained dual voltage transformer with a change-over switch which provides operation on either 110-120 volts, 50-60 cycles or 220-240 volts, 50-60 cycles. The switch is set for operation at 110-120 volts for this work. This instrument is the best available of its type and is reasonably accurate for this work.

The cell used is shown in Figure 6. It consists of a brass jacket with a cooling system drilled in the jacket walls. Two brass plates form the condenser. The larger plate is the high potential and is fastened rigidly to the cell with a ceramic insulator. A brass strip terminating in a banana plug connects it to the Q meter terminal. The smaller plate is fastened to a Vernier caliper which in turn is fastened to the cell directly. A banana plug connects the cell to the ground potential.

Variation of the caliper readings gives a corresponding change in the cell capacitance. For this work, the caliper was held rigid with tape. The cell is covered with a machined piece of brass which fits snugly and minimizes contact with moist air.



CROSS SECTION VIEW OF THE CELL USES FOR MEASURING DIELECTRIC CONSTANTS OF LIQUIDS AT RADIO FREQUENCIES

Figure 6

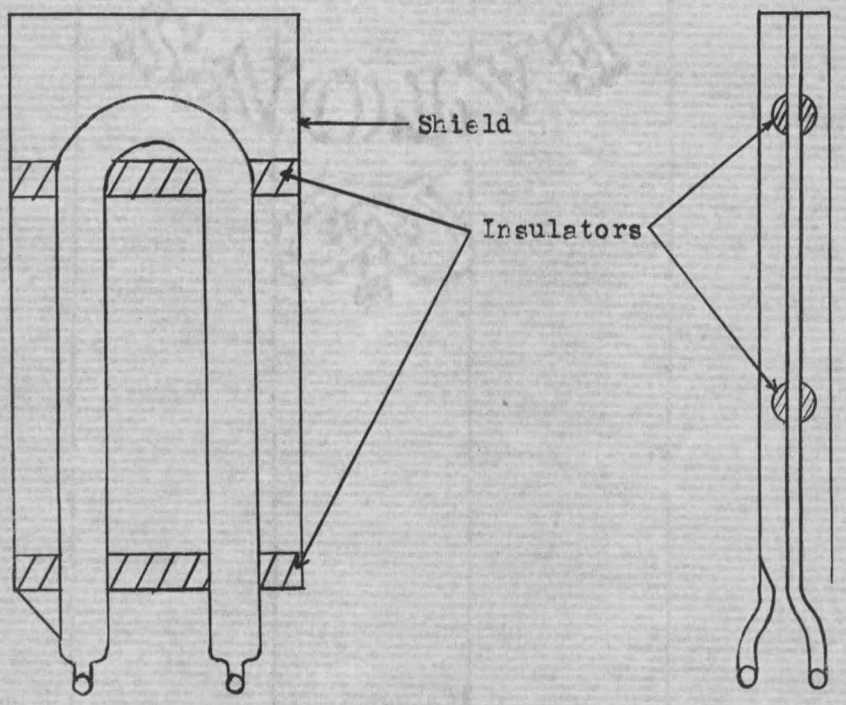
Two types of inductance coils were used. These are shown in Figure 7. The first type made consisted of a piece of ¼ inch copper tubing bent in the shape of a horseshoe and shielded with copper sheet bent to form a cylinder. One end was sealed with a piece of copper and the other with lucite, through which the coil terminals passed. The other type was made from coaxial cable of 3/8 inch outer diameter which was shorted with copper plate at one end. The nature of the construction of the cable produced an inherent shielding, quite sufficient for this purpose. Six coils were made varying in length, to cover the range of frequency from 30-120 megacycles. The three longer coils covering the range from 30 to 80 mc, were of the first type described above, because at those frequencies those coils gave the highest Q. Conversely, the three cells made from coaxial cables for the range 85 to 120 mc gave the highest values of Q. The absolute values of inductance for the coils were not determined.

The pump which was used to force the refrigerant through the cell was a standard Chevrolet oil pump which was powered by a 1/3 horsepower motor. It gave very satisfactory results even at temperatures below $-50^{\circ}C$.

The refrigerant was a mixture of acetone and dry ice which proved to be the least viscous liquid at temperatures to $-70^{\circ}C$.

(b) Methods of Calculation

According to Brotherton[4], in a practical capacitor, such as the cell used for measurements, the capacitance forms a series circuit with the inductance. A simple diagram of the circuit is shown in Figure 8.



CROSS SECTION VIEW OF THE TYPES OF COILS USED WITH THE Q METER

Figure 7

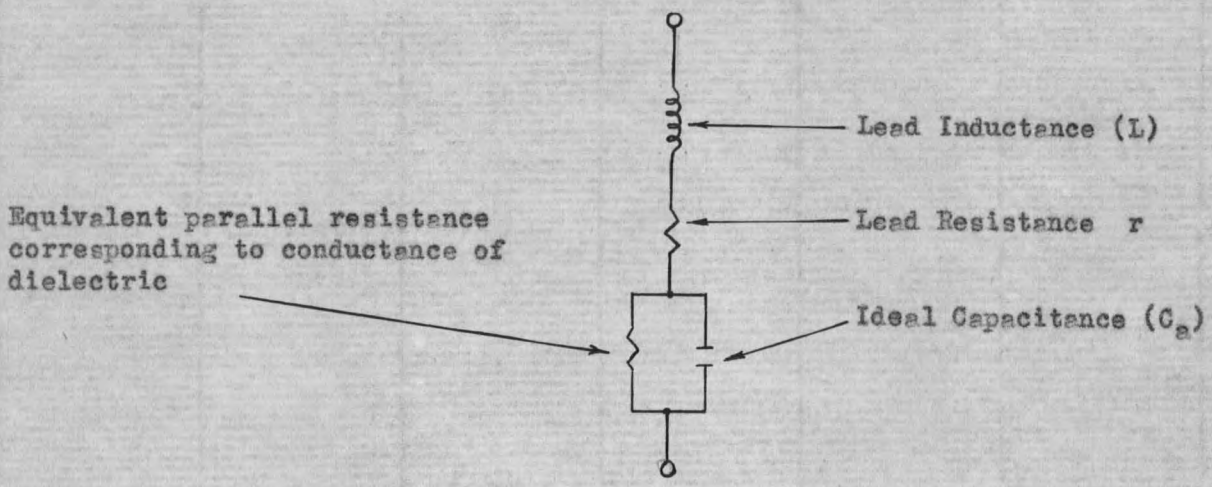


Figure 8

The impedence of this circuit will be:

$$Z = r + \frac{g}{g^2 + w^2C_a^2} - i\frac{wC}{g^2 + w^2C_a^2} + iwL$$

where r is the lead resistance, g is the conductance of the dielectric, w is $2\pi f$ where f is the frequency, C_a is the ideal or actual capacitance, L is the inductance. In practice g^2 is much smaller than $w^2C_a^2$ and the equation reduces to:

$$Z = r + \frac{g}{w^2C_a^2} + i\left(\frac{-1}{wC_a} + wL\right)$$

The positive reactance for the inductance X_L reduces the negative resistance appearing across the terminals by the amount equal to wL. The effect of this inductive element is, therefore, to increase the apparent capacitance as the frequency rises.

The reactance X_{C_e} measured for the circuit, at the terminals, is

$$-X_{C_e} = - X_{C_a} + X_L$$

since in the range below the resonance frequency the capacitive reactance is negative in sign.

X_{C_e} is equal to $\frac{1}{w\ Ce}$; $X_{C_a} = \frac{1}{wCa}$ and $X_2 = wL$

where Ca represents the ideal or actual capacitance and Ce the effective or measured capacitance.

So that the equation can be written:

$$- \frac{1}{wCe} = - \frac{1}{wCa} + wL$$

Multiplying through by wCe and wCa it becomes :

$$- wCa = - wCe + wCa\ wCe\ wL$$

This equation can be rearranged to become:

$$Ca = Ce - Lw^2CaCe$$

or

$$Ca = \frac{Ce}{1 + Lw^2Ce}$$

To use this equation to find the actual capacitance, the inductance must first be calculated by some other means. Since there are two unknowns, two equations are necessary to obtain the inductance. Two sets of conditions for the same equation may suffice, providing the unknowns remain constant over the range chosen. If measurements are taken at two different frequencies, which we will designate as f_1 and f_2, the two equations will be:

$$Ca = \frac{Ce_1}{1 + Ce_1Lw_1^2} \qquad \text{and} \qquad Ca = \frac{Ce_2}{1 + Ce_2Lw_2^2}$$

or rearranging:

$$Ca\ Ce_1\ Lw_1^2 - Ce_1 + Ca = 0$$

$$CaCe_2\ Lw_2^2 - Ce_2 + Ca = 0$$

dividing by Ca we obtain:

$$Ce_1\ Lw_1^2 - Ce_1 \frac{1}{Ca} + 1 = 0$$

$$Ce_2\ Lw_2^2 - Ce_2 \frac{1}{Ca} + 1 = 0$$

The solution of L may be obtained using determinants thus:

$$L = \frac{\begin{vmatrix} -Ce_1 & 1 \\ -Ce_2 & 1 \end{vmatrix}}{\begin{vmatrix} Ce_1 w_1^2 & -Ce_1 \\ Ce_2 w_2^2 & -Ce_2 \end{vmatrix}}$$

$$L = \frac{Ce_2 - Ce_1}{Ce_2 Ce_1 w_2^2 - Ce_2 Ce_1 w_1^2}$$

$$L = \frac{Ce_2 - Ce_1}{Ce_2 Ce_1\ 4\pi^2 (f_2^2 - f_1^2)}$$

where f is the frequency. The exact value for L cannot be obtained using this equation, since it appears that the inductance of the cell and leads does vary with the frequency. However, if short leads are used the amount of inductance is reduced. The inductance used in these measurements was obtained by calculating values for a difference of five megacycles, from 30 to 120 megacycles, then obtaining values for a difference of 10 megacycles over the same range. Repeating the process using a difference of 15, 20, 25, 30 and on up to 90 megacycles, and then averaging all of the values gave a result of approximately 5×10^{-8} henries. This value, when

used in the equation for actual capacitance, gave results for C_a which were in fair agreement. Tables V, VI and VII give the data and results of the calculation of the actual capacitance for the dielectrics, air, benzene and hexane over the range of frequencies from 30-100 megacycles at 25°C. The results are shown plotted against frequency in Figure 9.

TABLE V.

Actual Capacitance of the Cell with air as the Dielectric

f	C_e	w^2	L	C_o
31	13.661	3.79×10^4	5×10^{-8}	13.316
35	13.825	4.84		13.377
40	14.018	6.32		13.423
45	13.809	7.99		13.087
50	13.943	9.87		13.045
55	14.332	11.94		13.202
60	14.498	14.21		13.144
65	14.110	16.68		12.624
70	14.480	19.35		12.701
75	14.714	22.21	5×10^{-8}	12.647
80	15.093	25.27		12.676
85	15.495	28.52		12.690
75	14.383	22.21		12.402
80	14.681	25.27		12.384
85	15.032	28.52		12.378
90	15.561	31.98		12.461
95	15.936	35.63	5×10^{-8}	12.412
90	14.679	31.98		11.889
95	15.258	35.63		11.997
100	15.725	39.48		12.000

TABLE VI.

Actual Capacitance of the Cell with Benzene as the Dielectric

f	C_e	w^2	L	C_a
31	19.459	3.79×10^4	5×10^{-8}	18.767
35	19.679	4.84		18.785
40	20.025	6.32		18.833
45	19.815	7.99		18.361
50	20.316	9.87		18.464
55	20.800	11.94		18.502
60	------	----		------
65	20.853	16.68	5×10^{-8}	17.764
70	21.676	19.35		17.918
75	22.440	22.21		17.963
80	23.316	25.27		18.010
85	24.303	28.52		18.048
75	------	22.21		------
80	22.660	25.27		17.616
85	23.693	28.52		17.709
90	24.864	31.98		17.790
95	26.221	35.63	5×10^{-8}	17.873
90	23.549	31.98		17.108
95	24.958	35.63		17.277
100	26.496	39.48		17.397

TABLE VII.

Actual Capacitance of the Cell with Hexane as the Dielectric

f	C_e	w^2	L	C_a
31	17.790	3.79×10^4	5×10^{-8}	17.210
35	17.867	4.84		17.127
40	18.273	6.32		17.276
45	18.105	7.99		16.884
50	18.569	9.87		17.011
55	19.007	11.94		17.070
60	19.442	14.21		17.067
65	18.952	16.68	5×10^{-8}	16.365
70	19.778	19.35		16.601
75	20.313	22.21		16.574
80	21.057	25.27		16.631
85	22.012	28.52		16.753
75	19.597	22.21		16.095
80	20.377	25.27		16.204
85	21.359	28.52		16.372
90	22.322	31.98	5×10^{-8}	16.451
95	23.465	35.63		16.548
90	21.292	31.98		15.884
95	22.433	35.63		16.028
100	23.634	39.48		16.116

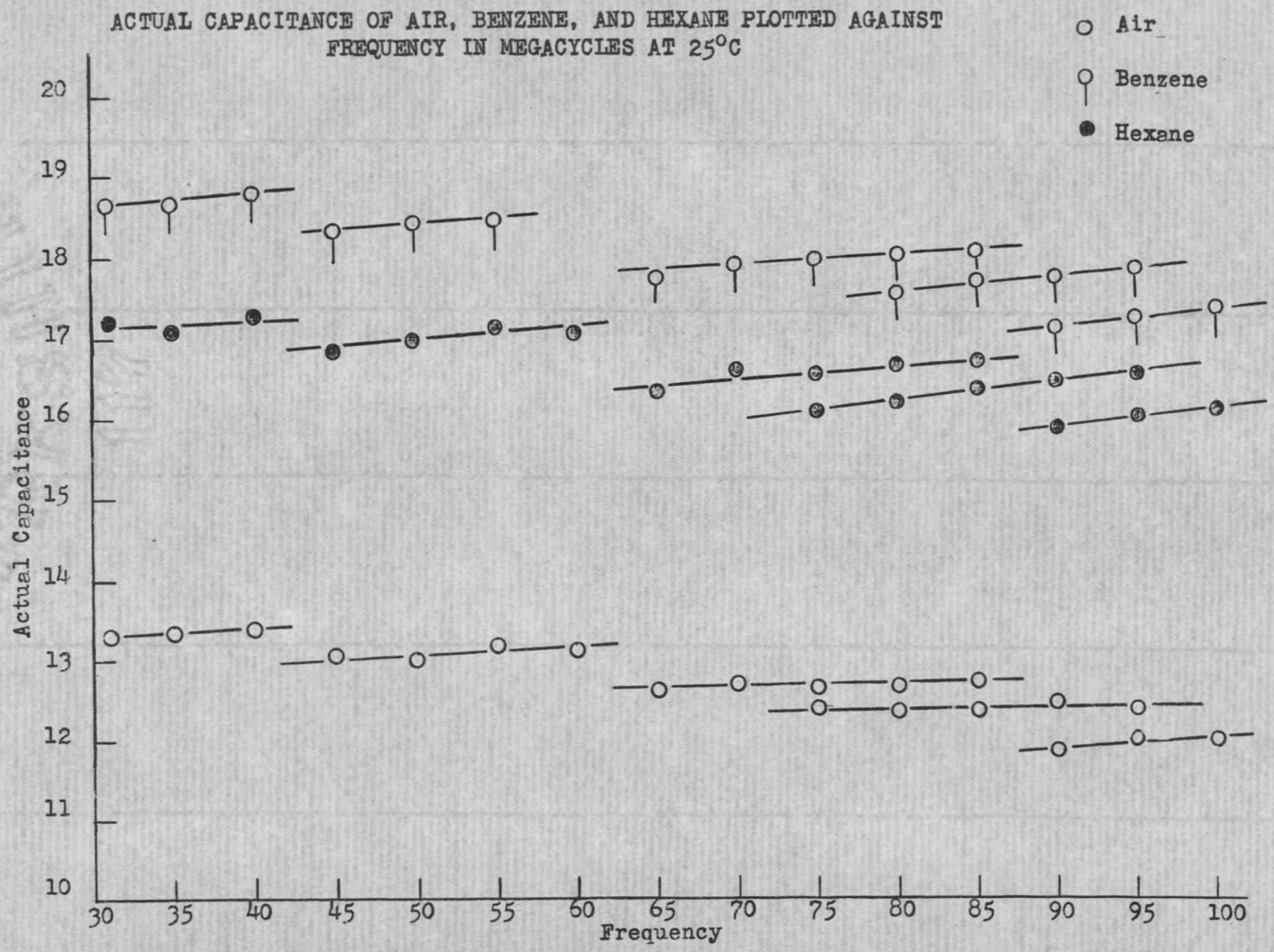

ACTUAL CAPACITANCE OF AIR, BENZENE, AND HEXANE PLOTTED AGAINST FREQUENCY IN MEGACYCLES AT 25°C
Air
Benzene
Hexane
Actual Capacitance
20
19
18
17
16
15
14
13
12
11
10
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
Frequency

Figure 9

The cell constant was obtained in the following manner: The total capacitance of the cell with the dielectric will be equal to the sum of the lead capacitance and the product of the dielectric constant of the dielectric and the capacitance between the two plates and the plates and cell. If air is the dielectric, $C_a = C_o + \epsilon_a C$. C is also called the cell constant. If a non-polar liquid of known dielectric constant is placed in the cell, the total capacitance becomes equal to the sum of the lead capacitance and the product of the dielectric constant of the known liquid and the cell constant. Thus: $C_x = C_o + \epsilon_x C$. If the equation for the capacitance of the cell with air is subtracted from the equation for the capacitance of the cell with the known liquid it is noted that $C = \frac{C_x - C_a}{\epsilon_x - \epsilon_a}$ and $x = \frac{(C_x - C_a + \epsilon_a C)}{C}$. Using pure benzene with a dielectric constant of 2.273 at 25°C, the cell constant was calculated over the range of frequencies from 30-100 mc. The results of the calculation are shown in Table VIII and are shown plotted against frequency in Figure 10.

Again the values are not exactly constant, but are in close agreement in most cases. The average value is 4.19.

TABLE VIII.

Cell Constant

f	C_B	C_A	ϵ_B	ϵ_A	C
31	18.767	13.316	2.273	1	4.282
35	18.785	13.377			4.248
40	18.833	13.423			4.250
45	18.361	13.087			4.143
50	18.464	13.045			4.257
55	18.502	13.202			4.163
60	------	------			-----
65	17.764	12.624			4.038
70	17.918	12.701			4.099
75	17.963	12.647			4.176
80	18.010	12.676			4.190
85	18.048	12.690	2.273	1	4.209
75	------	------			-----
80	17.616	12.384			4.110
85	17.709	12.378			4.188
90	17.790	12.461			4.186
95	17.873	12.412			4.290
90	17.108	11.889			4.100
95	17.277	11.997			4.148
100	17.397	12.000			4.240

C_B is actual capacitance of benzene
C_A is actual capacitance of air

CELL CONSTANT PLOTTED AGAINST FREQUENCY IN MEGACYCLES

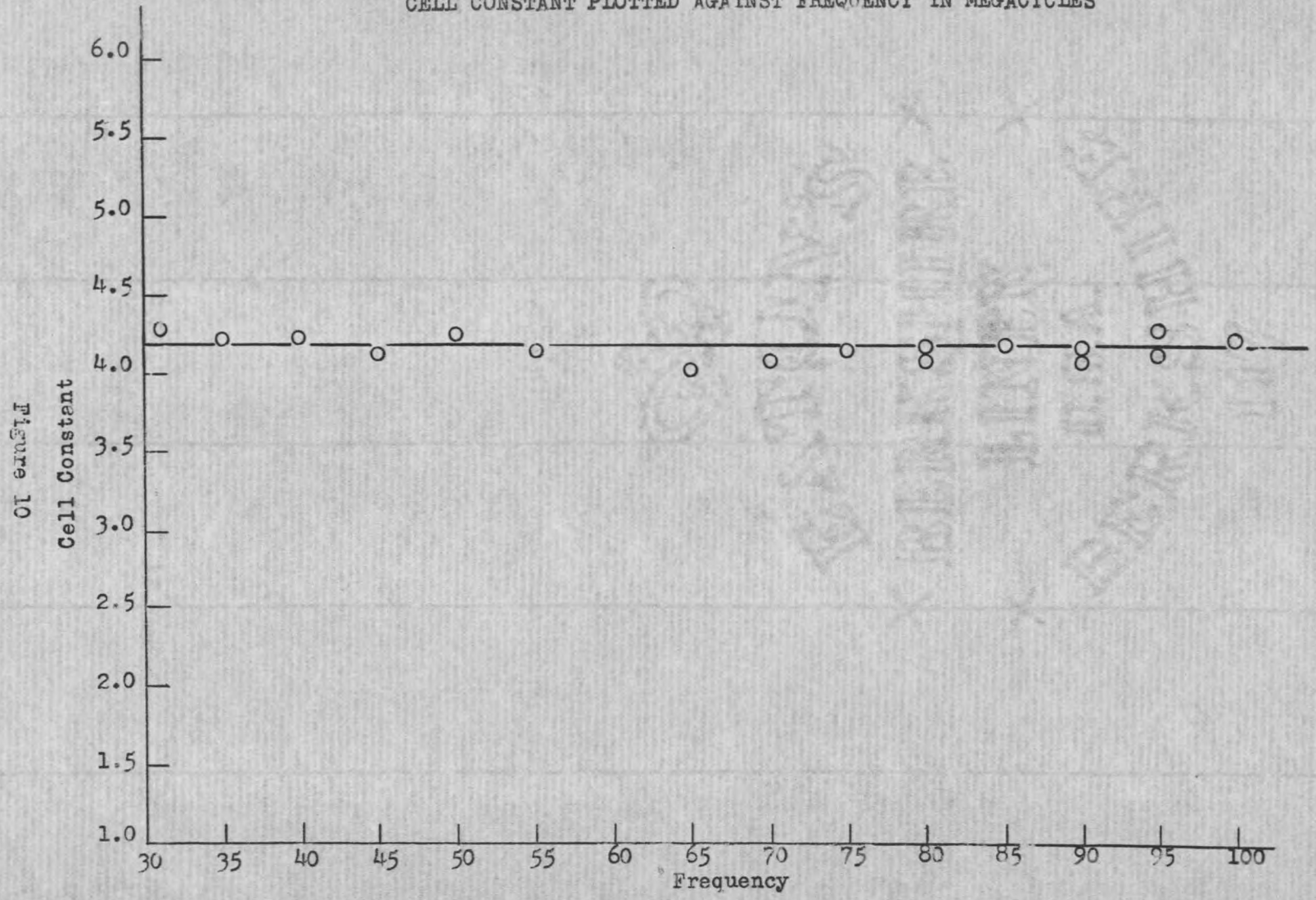


Figure 10

(c) Difficulties Encountered

When this work was begun the Q meter had just arrived from the factory and very little was known of its limitations. There were no coils available which would give a small enough inductance for this work, so that all the coils had to be made. It was found that copper tubing of $\frac{1}{4}$ inch diameter gave high Q meter readings over the range of frequencies used. The Q values, however, decreased with increasing frequency. Calculations based on readings obtained for capacitance of the cell with dielectric using unshielded coils did not show good agreement. The deviation was thought to be caused by a capacitance between the unshielded coil and the cell. However, the deviations persisted even after shielding the coils. The inductance, previously calculated using the equation derived on page 47 with a frequency difference of 5 megacycles only, was recalculated in the manner described on page 48. This seemed to bring the values within the range of experimental error. The curves shown in Figure 9 were drawn to show the effect for each coil used. No explanation has been found for this deviation from what should be a continuous straight line or a smooth curve. It was thought that the deviation might be due to the type of coil used, but coils made from coaxial cable which are inherently shielded made no difference. It is possible that the internal leads, that is, those within the instrument are the cause, but that possibility has not been investigated thoroughly as yet.

(d) Dielectric Constant of Titanium Tetraethylate in the range of frequencies from 30 to 95 megacycles at various temperatures

The dielectric constant is calculated using the equation:

$$\epsilon_x = \frac{C_x - C_a + \epsilon_a C}{C}$$

given on page 57.

Results obtained for calculations using data obtained at 25°C are given in Table IX, and shown plotted against frequency in Figure 11. The results at 25°C indicate that anomalous dispersion does not appear within the frequency range 30-100 megacycles at that temperature.

It was found that the compound becomes very viscous at low temperatures by Crowe. It is a known fact that for liquids exhibiting a high viscosity, the anomalous dispersion occurs at lower frequencies than in a liquid of lower viscosity. Keeping that in mind, measurements were made at temperatures of 6°C, -30°C, -43°C and -54°C, using the cooling apparatus described on page 47. The temperature variation was ±1° at 6°C and ± 2°C at lower temperatures.

Results of the calculations are given in Tables X, XI, XII and XIII. The results are shown plotted against frequency in Figures 12, 13, 14 and 15. Figure 15 shows a definite decrease of the dielectric constant until the frequency 55 mc was reached at which frequency it increases sharply until the value obtained at other temperatures is again maintained. If the decrease shown was anomalous dispersion, occurring at that low frequency at -54°C, it should also apparently appear at a higher frequency at -43°C.

No further measurements were possible, however, due to failure of the circulating system.

TABLE IX.

Dielectric Constant of $Ti(OC_2H_5)_4$ at 25°C

f	C_{Ti}	C_A	C	ϵ_A	ϵ_{Ti}
31	24.803	13.316	4.193	1	3.740
35	24.946	13.377			3.759
40	24.967	13.423			3.753
45	24.473	13.087			3.715
50	24.643	13.045			3.766
55	24.698	13.202			3.742
65	23.978	12.624			3.708
70	24.118	12.701	4.193	1	3.723
75	24.217	12.647			3.759
75	23.851	12.402			3.730
80	23.990	12.384			3.768
85	24.213	12.378			3.823
90	23.649	11.889			3.805
95	24.003	11.997			3.863

C_{Ti} Actual capacitance of tetraethoxytitanium

DIELECTRIC CONSTANT OF TETRAETHOXYTITANIUM PLOTTED AGAINST FREQUENCY IN MEGACYCLES AT 25°C

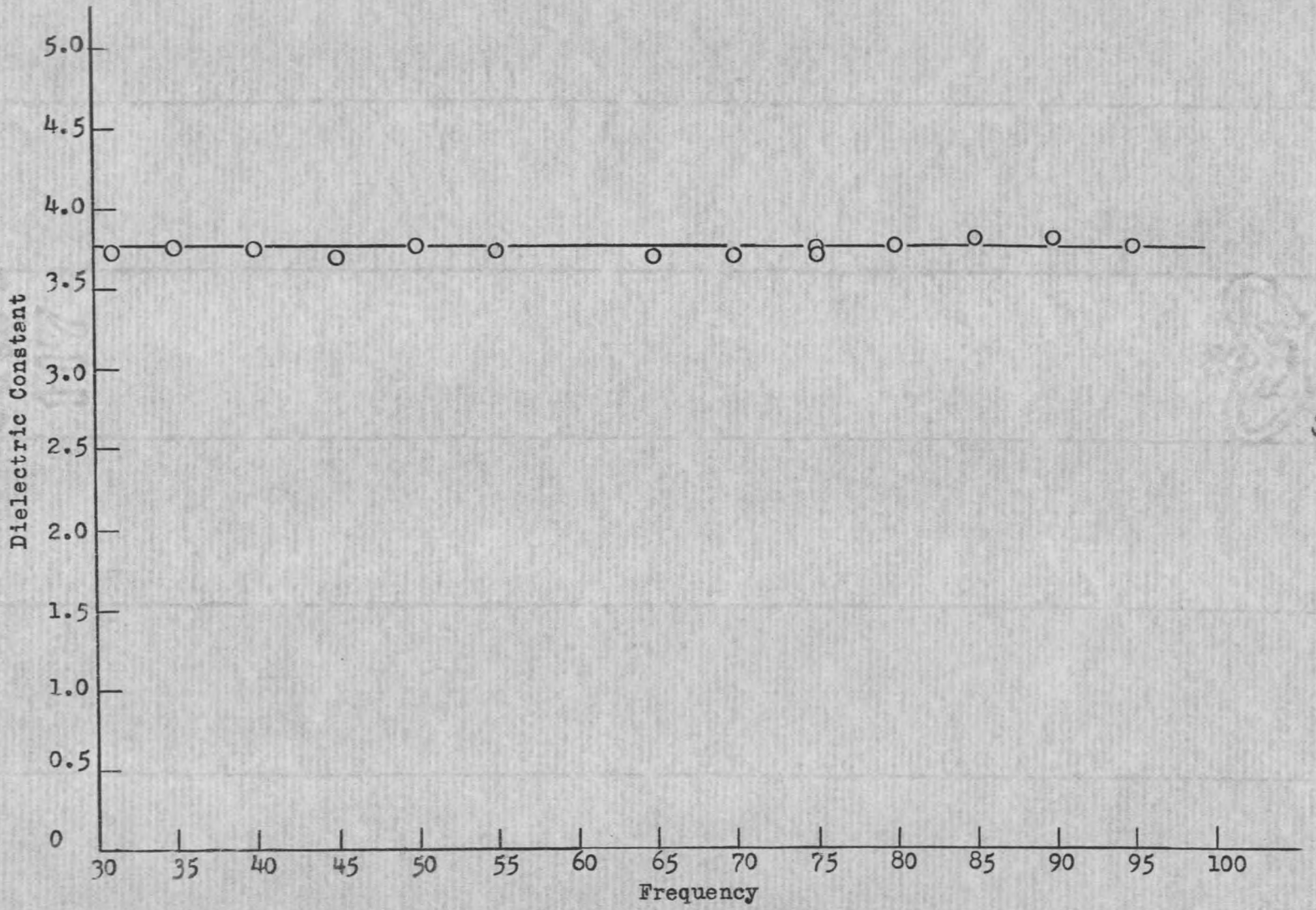


Figure 11

TABLE X.

Dielectric Constant of $Ti(OC_2H_5)_4$ at 6°C

f	C_{Ti}	C_A	C	ϵ_A	ϵ_{Ti}
31	25.032	13.316	4.193	1	3.794
35	25.135	13.377			3.804
40	25.182	13.423			3.804
45	24.573	13.087			3.739
50	24.702	13.045			3.780
55	24.723	13.202			3.748
65	24.151	12.624			3.749
70	24.418	12.701	4.193	1	3.794
75	24.442	12.647			3.813
75	23.926	12.402			3.748
80	24.046	12.384			3.781
85	24.236	12.378			3.828
90	23.596	11.889			3.792
95	23.985	11.997			3.859

TABLE XI.

Dielectric Constant of $Ti(OC_2H_5)_4$ at -30°C

f	C_{Ti}	C_A	C -	ϵ_A	ϵ_{Ti}
31	24.816	13.316	4.193	1	3.743
35	24.949	13.377			3.760
40	24.868	13.423			3.730
45	24.610	13.087			3.748
50	24.650	13.045			3.768
55	24.714	13.202			3.746
65	24.018	12.624			3.717
70	24.209	12.701	4.193	1	3.745
75	24.388	12.647			3.800
75	23.878	12.402			3.737
80	24.071	12.384			3.787
85	24.342	12.378			3.853
90	23.883	11.889			3.860
95	24.291	11.997			3.932

TABLE XII.

Dielectric Constant of $Ti(OC_2H_5)_4$ at -43°C

f	C_{Ti}	C_A	C	ϵ_A	ϵ_{Ti}
31	24.634	13.316	4.193	1	3.699
35	------	13.377			-----
40	24.722	13.423			3.695
45	24.293	13.087			3.673
50	24.473	13.045			3.725
55	24.493	13.202			3.693
65	23.841	12.624			3.675
70	24.057	12.701	4.193	1	3.708
75	21.164	12.647			
75	23.733	12.402			3.702
80	23.920	12.384			3.751
85	24.282	12.378			3.839
90	23.700	11.889			3.817
95	24.024	11.997			3.868

TABLE XIII.

Dielectric Constant of $Ti(OC_2H_5)_4$ at -54°C

f	C_{Ti}	C_A	C	ϵ_A	ϵ_{Ti}
31	24.628	13.316	4.193	1	3.698
35	24.695	13.377			3.699
40	24.698	13.423			3.689
45	24.153	13.087			3.639
50	23.324	13.045			3.451
55	23.414	13.202			3.435
65	23.885	12.624			3.686
70	24.015	12.701	4.193	1	3.698
75	24.151	12.647			3.744
75	23.669	12.402			3.687
80	23.882	12.384			3.742
85	24.121	12.378			3.801
90	23.721	11.889			3.822
95	24.133	11.997			3.894

DIELECTRIC CONSTANT OF TETRAETHOXYTITANIUM PLOTTED AGAINST FREQUENCY IN MEGACYCLES AT 6°C

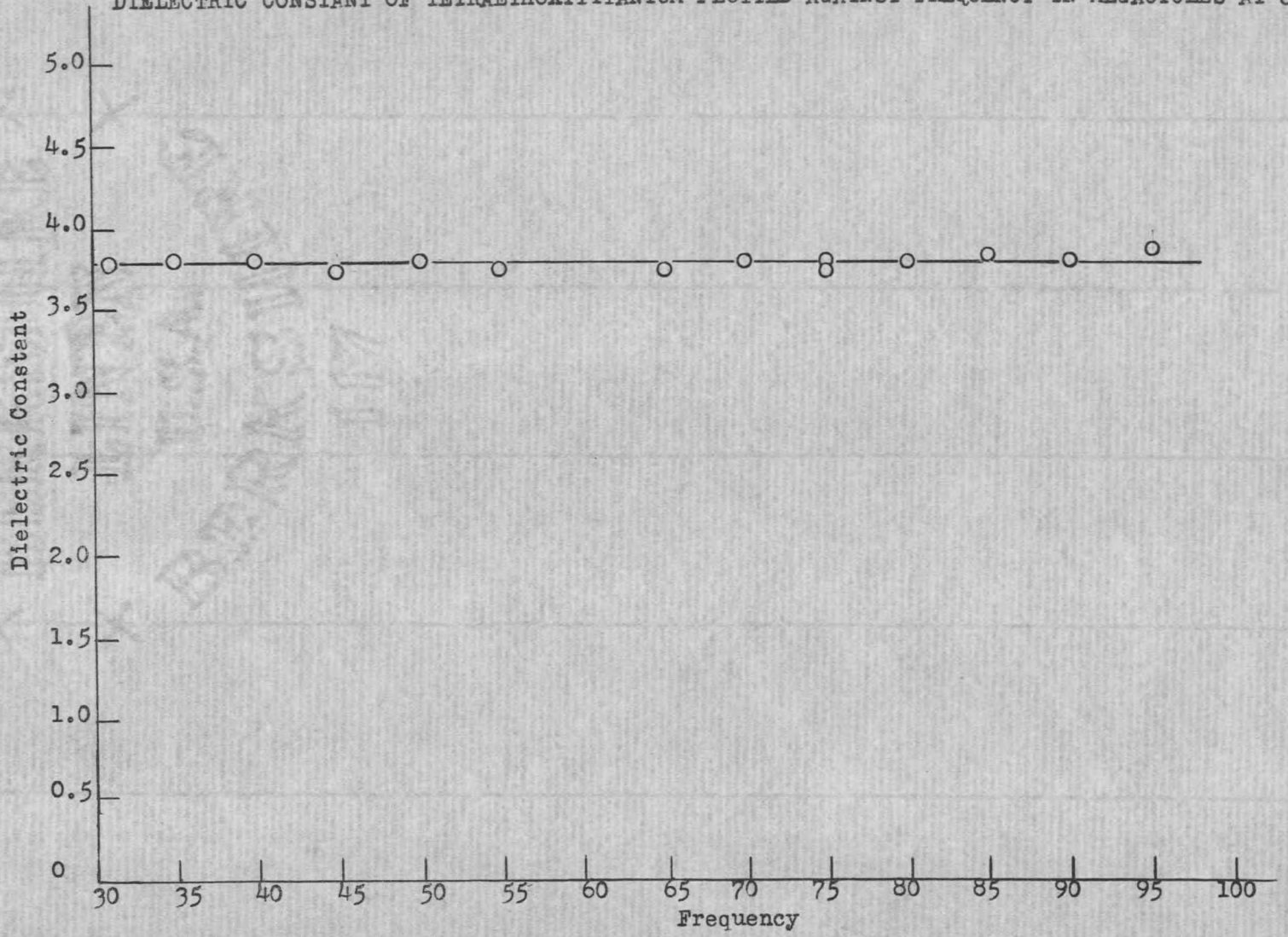


Figure 12

DIELECTRIC CONSTANT OF TETRAETHOXYTITANIUM PLOTTED AGAINST FREQUENCY IN MEGACYCLES AT -30°C

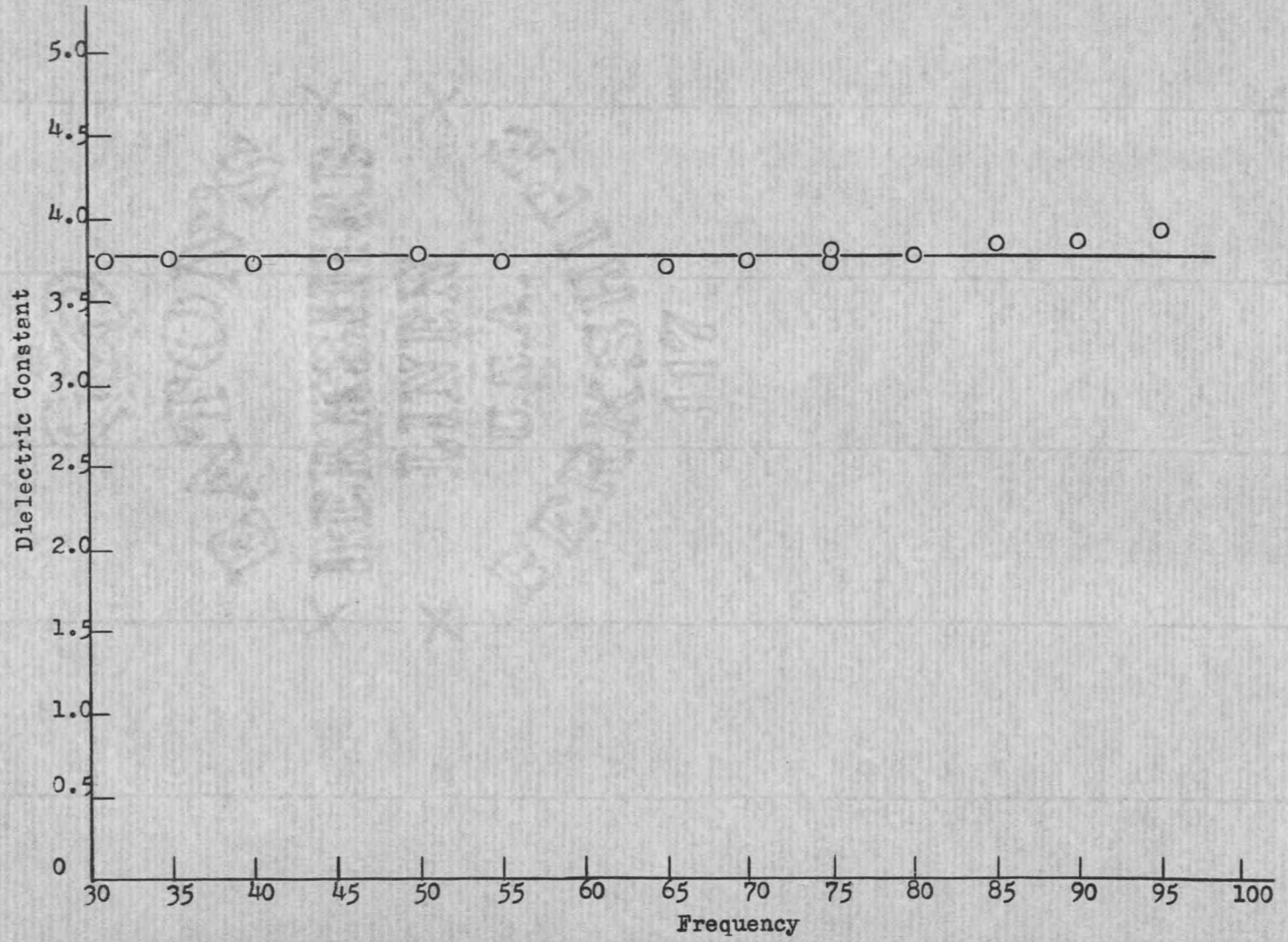


Figure 13

DIELECTRIC CONSTANT OF TETRAETHOXYTITANIUM PLOTTED AGAINST FREQUENCY IN MEGACYCLES AT -43°C

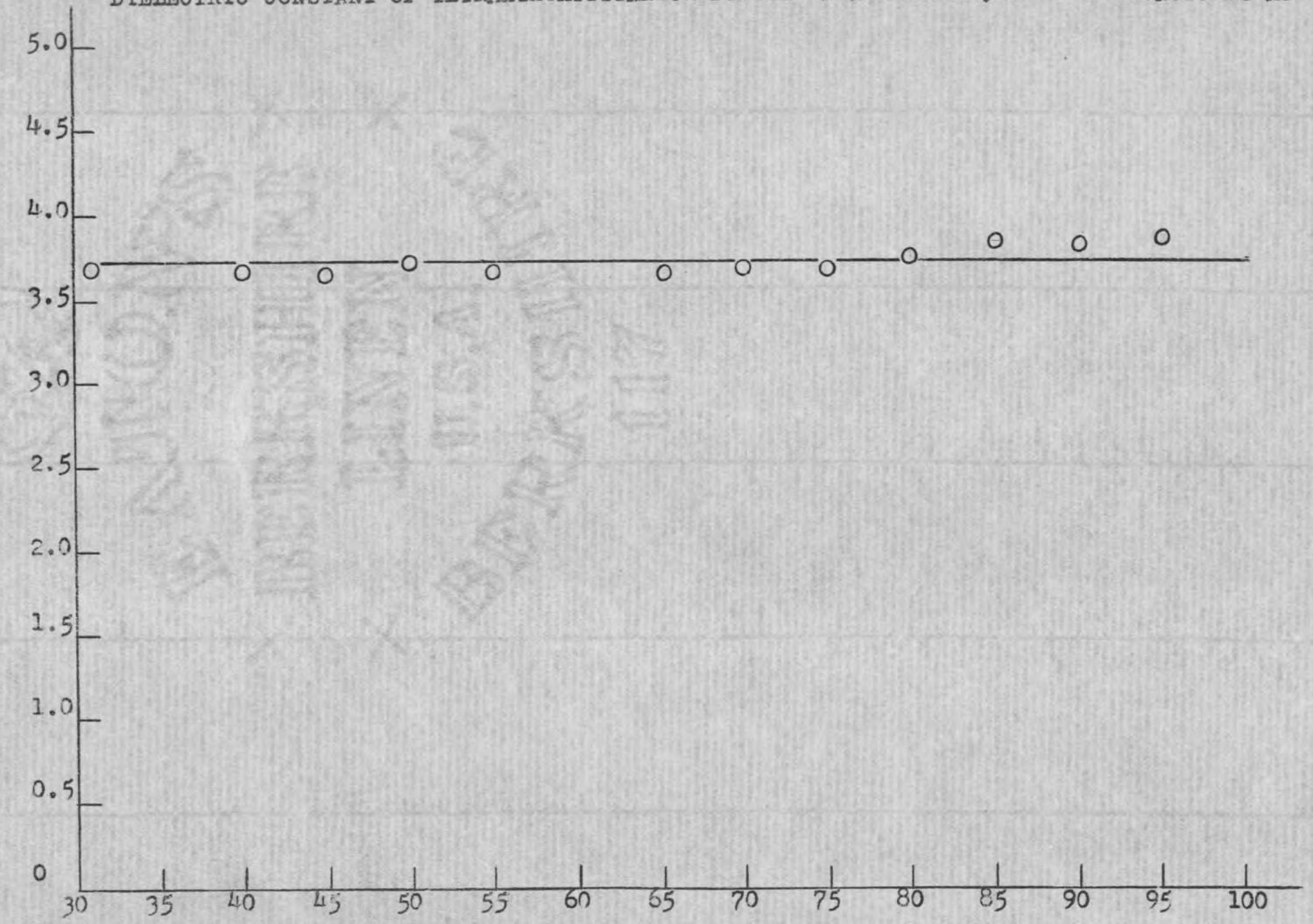


Figure 14

DIELECTRIC CONSTANT OF TETRAETHOXYTITANIUM PLOTTED AGAINST FREQUENCY IN MEGACYCLES AT -54°C

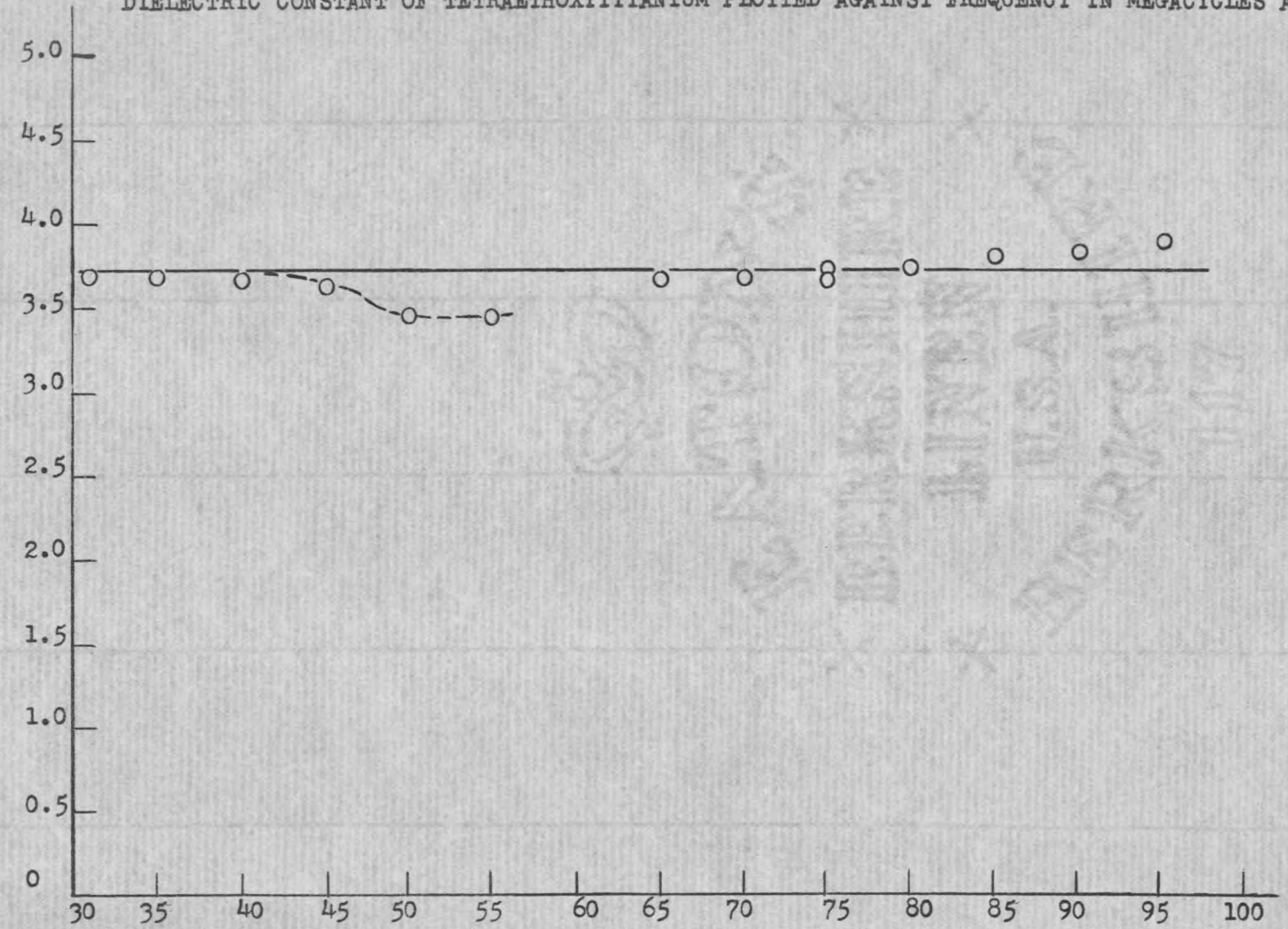


Figure 15

XVI. SPECIFIC CONDUCTIVITY OF MONOCHLOROTRIETHOXYTITANIUM AT 25°C

An attempt was made to measure the capacitance and calculate the dielectric constant of monochlorotriethoxytitanium at a frequency of 1000 cycles at 25°C on a G. R. capacitance bridge, as well as at high frequencies. The capacitance of the cell, with monochlorotriethoxytitanium as the dielectric, could not be measured on the bridge at that frequency, although the dielectric constant appeared to be about 8 to 10, as shown by an approximate measurement at 4.6 mc on the instrument used by Crowe.

Very few pure liquids and, generally only those which are ionic, conduct electricity. This conductance appears to be the reason for the inability to obtain capacitance readings.

The specific conductivity of pure monochlorotriethoxytitanium at 25°C was 1.4×10^{-6} mhos, measured with a Wheatstone Bridge at 1000 cycles/sec. This is about the same as that of pure water.

XVII. DISCUSSION OF EXPERIMENTAL RESULTS

Although the results for the dielectric constant show deviations from a constant value over the range of frequency, no anomalous dispersion was indicated for certain. The values for the dielectric constant at -54°C may have shown the start of the dispersion effect at about 55 megacycles, but the results are still somewhat doubtful.

The capacitance change with each different coil leaves some doubt in regard to the reliability of the data. The values at various frequencies, for a single coil fall on a straight line, but for different coils, at the same frequency, the capacitance was different and the difference varied for each dielectric used. After considerable study of this problem, it appears that coils and external leads are probably not the cause, but residual constant resistance, capacitance, and inductance within the instrument may be the cause. The variation however is small and almost within the expected precision of the instrument.

The frequency at which anomalous dispersion will become evident is related to the time of relaxation for the liquid by the equation $w = \frac{1}{\tau}$. Solving this relationship for τ using the value of 95 megacycles for the frequency, it can be seen that τ cannot exceed 1.68×10^{-9} seconds.

Monochlorotriethoxytitanium, for which a partial ionic bond between the chlorine and titanium atom has been proposed, does conduct electricity. The specific conductivity measurements indicate that the compound has about the same conductivity that pure water exhibits.

It was for that reason that the attempt to measure the dielectric constant was not successful on the instruments available.

XVIII. SUMMARY

1. Tetraethoxytitanium was prepared and purified and the dielectric constant of the pure liquid was studied at frequencies ranging from 30-100 megacycles and at temperatures from -50°C to 25°C.

2. The dielectric constant does not decrease with increasing frequency within the range of measurements and therefore does not exhibit anomalous dispersion at those temperatures and frequencies.

3. The time of relaxation cannot exceed 1.68×10^{-9} sec.

4. Monochlorotriethoxytitanium was prepared and purified and an attempt made to measure the dielectric constant at a frequency of 1000 cycles and a temperature of 25°C. Monochlorotriethoxytitanium conducts electricity and the dielectric constant was not obtained.

5. The specific conductivity of pure monochlorotriethoxytitanium was measured at 25°C and found to be 1.34×10^{-6} reciprocal ohms.

6. A discussion of the difficulties involved in the calibration and use of a Q meter is presented.

XIX. ACKNOWLEDGMENT

The author wishes to take this opportunity to express his sincerest appreciation and thanks to Dr. Charles N. Caughlan for his personal guidance and inspiration during this research, to Mr. R. C. Seibel of the Electrical Engineering Department, and to the other members of the Chemistry Department for their many helpful suggestions. He also wishes to thank the Research Corporation of New York for making this investigation possible through a grant.

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