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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Montana State University

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 $TiClH_{12}C_5O_4$ based on one Ti atom, or $C_6H_{15}O_5$ 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 10.9×10^{-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 $TiCl(OC_2H_5)_3$ in glycol and found to be more like $TiCl(OC_2H_5)_3$.

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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TABLE OF CONTENTS

PART 1.

		Pg.
I.	ABSTRACT	4
II.	INTRODUCTION	5
III.	REACTION OF TITANIUM TETRACHLORIDE WITH ETHYLENE GLYCOL	8
IV.	ANALYSIS OF THE COMPOUND	9
	For Titanium	9
	For Chlorine	9
	For Carbon and Hydrogen	10
V.	MOLECULAR WEIGHT DETERMINATION	12
VI.	CONDUCTIVITY MEASUREMENTS	14
VII.	OTHER COMPOUNDS MADE	18
VIII.	DISCUSSION OF THE EXPERIMENTAL RESULTS	20
IX.	SUMMARY	22

PART 2.

X.	ABSTRACT	23
XI.	INTRODUCTION	24
XII.	LITERATURE SURVEY	26
XIII.	THEORETICAL DISCUSSION	27
XIV.	PREPARATION OF THE COMPOUNDS	42
XV.	MEASUREMENT OF THE DIELECTRIC CONSTANT OF TETRAETHOXYTITANIUM AT VARYING TEMPERATURES AND FREQUENCIES	43
	(a) Apparatus used for measurements	43
	(b) Methods of Calculation	47
	(c) Difficulties encountered	60

Pg.

XV. (Continued)

(d) Dielectric constant of tetraethoxytitanium at varying frequency and temperature 60

XVI. SPECIFIC CONDUCTIVITY OF MONOCHLOROTRIETHOXYTITANIUM AT 25°C. 72

XVII. DISCUSSION OF EXPERIMENTAL RESULTS 73

XVIII. SUMMARY. 74

XIX. ACKNOWLEDGMENTS. 75

XX. LITERATURE CITED AND CONSULTED 76

Part I.

I. ABSTRACT

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 chlorine, 5.34 percent hydrogen, 26.92 percent carbon and 29.23 percent oxygen. The empirical formulae calculated from these data are $TiClH_{12}C_5O_4$ based on one Ti atom, or $C_6H_{15}O_5TiCl$ based on 6 carbon atoms.

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

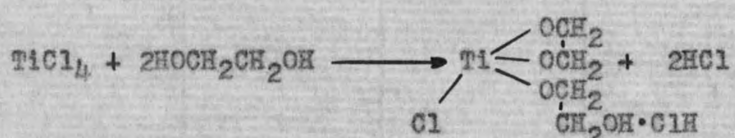
The conductivity of a solution of the product of the reaction between ethylene glycol and titanium tetrachloride was measured. A concentration of four grams of solute in 1000 grams of ethylene glycol exhibited a specific conductivity of 10.9×10^{-5} reciprocal ohms. The specific conductivity was found 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 $TiCl(OC_2H_5)_3$ in glycol and found to be more like $TiCl(OC_2H_5)_3$.

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 monochlorotriethoxytitanium with ethylene glycol. Its properties were not tested since it was also decomposed by heat and with time.

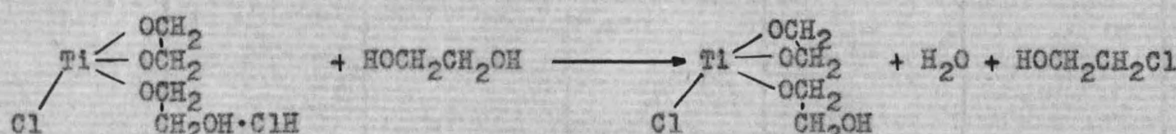
The apparatus used for analysis is described and an attempt made to explain the experimental results.

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. 

and on further heating:

2. 

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.

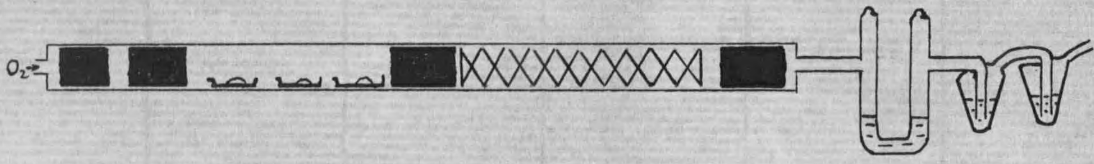


Figure 1

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°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.

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

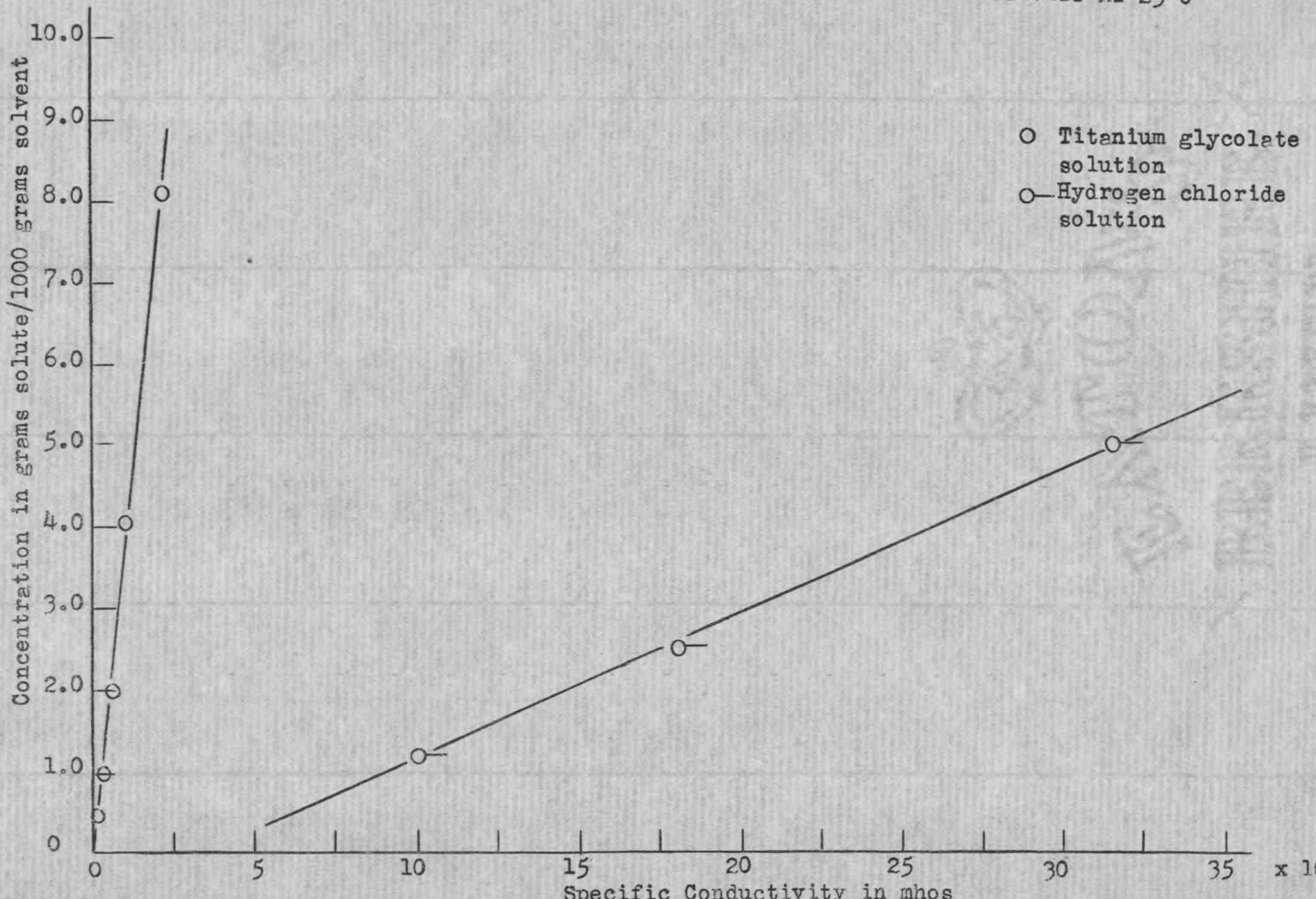


Figure 2

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

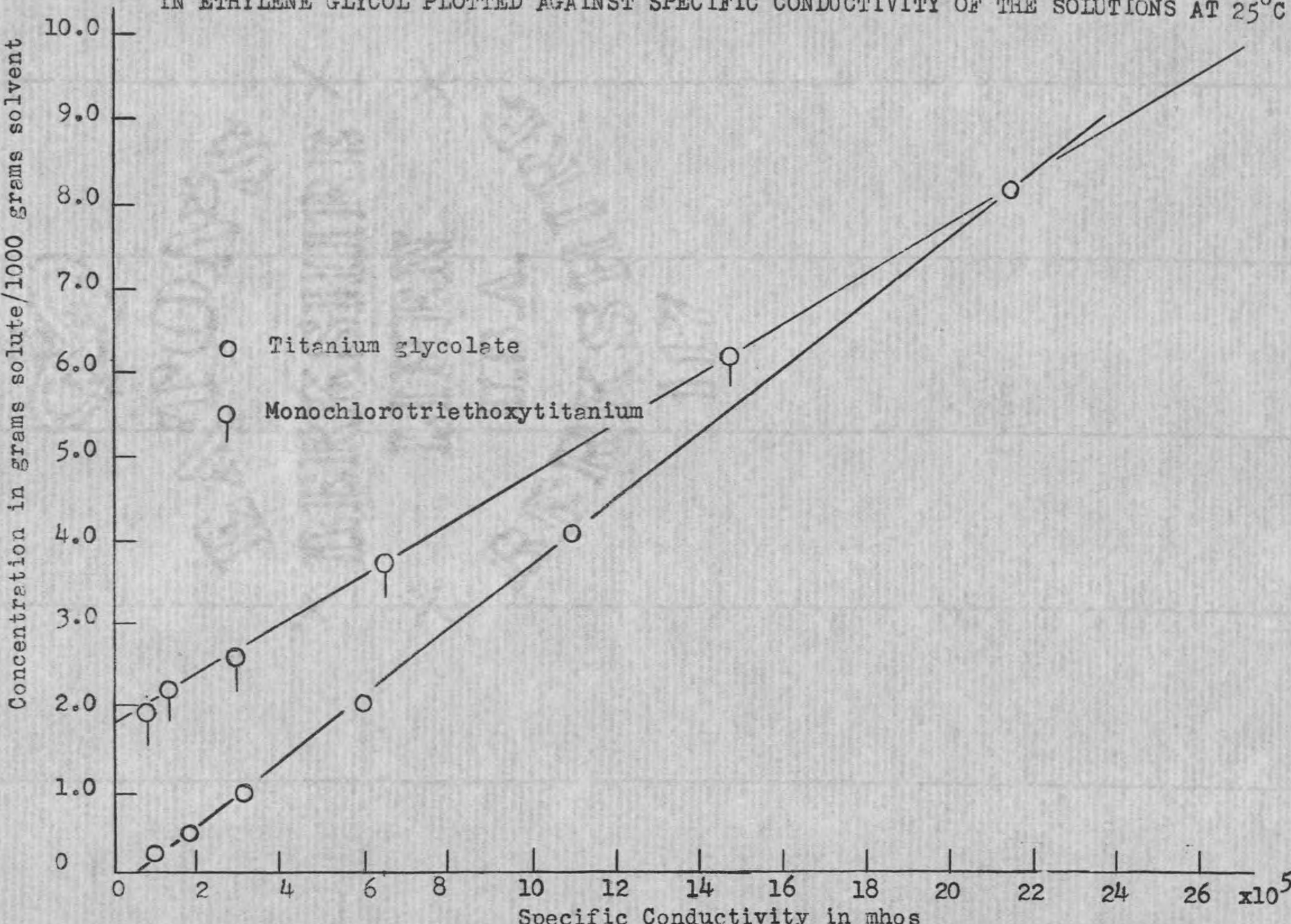


Figure 3

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.

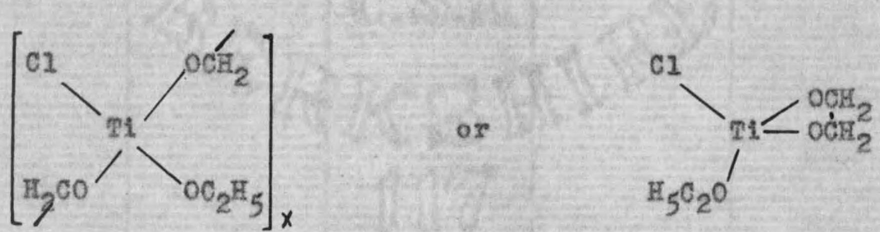
The odor and a boiling point indicated the volatile substance was ethyl alcohol, which in turn indicated that the second possibility shown above took place. The residue was a very viscous, clear, colorless liquid which solidified when the pressure was reduced in the flask. The white solid was powdered 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

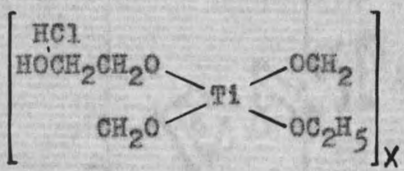
Good agreement was obtained between different samples in the analysis of the compound described in Section IV for titanium. This indicated that the product is quite uniform. Repeated attempts at making the compound, produced slightly different results in each case. That would seem to indicate several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

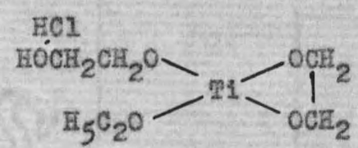
There is no proof that the above type of reaction takes place with the titanium compound. However it has been demonstrated with the reaction of monochlorotriethoxytitanium with glycol, that one or more ethyl groups on the molecule have been replaced by the glycol. The analytical data and empirical formula 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:



or



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.