The physical properties of organic titanates
by Howard M Smith

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
Montana State University

Abstract:
A study has been made of the molar polarizations of titaniumtetra-ethylate at temperatures ranging from 20°C to -60°Co' The values obtained were practically constant at these temperatures, The values ranged from 114.6 cc/mole at. 17°C to 112.3 cc/moIe at -60°C.

The associations of titaniumtetrapropylate, titaniumtetrabutylate, and monochloro-triethoxy-titanium, have been measured in dilute solution in benzene and have been found to be approximately three.

Pure crystals of titaniumtetraethylate were prepared and, identified as being monoclinic. The compound was optically biaxial and its indices of refraction were: n beta (y) 1.601 more or less, n alpha (x) 1.591 or less, n gamma (z) l.608 or more. The determination of n alpha and n gamma are only approximate.

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I. ABSTRACT

A study has been made of the molar polarizations of titaniumtetraethylate at temperatures ranging from 20°C to -60°C. The values obtained were practically constant at these temperatures. The values ranged from 114.6 cc/mole at 17°C to 112.3 cc/mole at -60°C.

The associations of titaniumtetrapropylate, titaniumtetrabutylate, and monochloro-triethoxy-titanium, have been measured in dilute solution in benzene and have been found to be approximately three.

Pure crystals of titaniumtetraethylate were prepared and identified as being monoclinic. The compound was optically biaxial and its indices of refraction were: n beta (y) 1.601 more or less, n alpha (x) 1.591 or less, n gamma (z) 1.608 or more. The determination of n alpha and n gamma are only approximate.

II. INTRODUCTION

Physical properties and structures of inorganic titanates have been known for some time but very little is known about the organic derivatives of $TiCl_4$.

Some inorganic titanates possess very large dielectric constants and as such are exceptional dielectric materials. In view of this fact it was decided to study organic derivatives of $TiCl_4$ in order to find out more about their dielectric behavior. Crowe (1) succeeded in showing that there was nothing unusual in the dielectric properties of these organic compounds at ordinary temperatures; however Katz's (2) work with the polarization of titaniumtetraethylate at lower temperatures indicated some interesting structural implications. Some restricted rotation was indicated and it was the purpose of the present work to verify this information. Katz also succeeded in preparing irregular crystals of titaniumtetraethylate which were to be used in X-ray diffraction measurements and determination of crystal habit. Since this had not been accomplished it was also desirable to prepare regular crystals if possible to obtain this information.

In addition a study of the association of several of these organic derivatives would add a valuable information regarding the nature and structure of the compounds and the bonds involved.

III. LITERATURE SURVEY

A great advance concerning the structure of molecules has been made during the past few years through the field of dielectrics. The electrical symmetry or asymmetry of molecules can be determined through these studies. Probably the best information obtainable on this subject is Debye's "Polar Molecules" (3) and Smyth's "Dielectric Constant and Molecular Structure" (4). There are some modifications on the above treatises such as Onsager's (5) modification of Debye's theory; however, there is a large amount of work that remains to be done in this field.

The literature has little or no information regarding the dielectric or other physical properties of organic titanium compounds. A thorough literature search on the part of Crowe (1) and Katz (2) has revealed that practically nothing is known about the organic esters of $TiCl_4$.

There is some information on the preparation of these compounds. The information that has been used most extensively in this manner is that of Bischoff and Adkins (6) and Jennings, Wardlow, and Way (7).

IV. THEORY AND POSSIBILITIES

Ordinarily it would not be permissable to leave out a theoretical discussion on the relationship between dielectrics and molecular structure. However, since this has been adequately discussed in Crowe's thesis (1) it appears justifiable to refer the reader to this work and to substitute in its place a discussion about the relationship between dielectrics and molecular association.

Liquids may be classified as normal or abnormal, the normal being those whose properties conform to certain laws, and the abnormal being those whose properties deviate from their laws. The use of Trouton's rule and the Eotvos-Ramsay-Shields constant may be mentioned as particularly common methods of classification. Abnormality is attributed to molecular association, a term which implies an aggregation of single molecules into complexes containing two or more of the single molecules. The extent of the supposed association is measured by the association factor which is the average number of single molecules in the actually existing molecules of the substance. Thus, if all the single molecules have combined to form double molecules the association factor is 2. If all the single molecules combine to form aggregates of three, the factor is 3. The degree of association is, of course, the fraction of the single molecules which have formed aggregates. It is customary to calculate the association factor from the deviation of the property under examination from the simple law supposed to apply to normal liquids. A phenomenon which causes a deviation in one property is apt to cause deviation in another as well; liquids which are found abnormal by one method are usually found abnormal by others.

The cause of molecular association is probably in the stray electrical forces associated with unsaturated or secondary valences which arise from local dipoles in the molecules, in the forces due to molecular dipoles which vary inversely as the third power of the distances from the centers of the dipoles, and from van der Walls forces. However, the forces exerted by dipoles are much more important than those exerted by van der Waals forces.

The total polarization P, is made up of three parts; the electronic polarization P_e, the atomic polarization P_a, and the polarization due to the permanent moment P_m. It can be shown (4) that the induced or distortion polarization, $P_e + P_a = 4\pi N\alpha_o/3$, where N is Avogadro's Number. α_o is the moment induced in a single molecule by unit electric field. It can also be shown that $\alpha_o = \sum e^2/f$, where f is a proportionality constant which determines the restoring force exerted upon the charge e when it is displaced a distance x by the action of a field. If the refractive index n, were determined at wave lengths too short for orientation polarization P_m to occur, then the molar refraction would not contain the contribution of the shifts of atoms or radicals in the field of the light wave. Therefore, the electronic polarization $P_e = (n^2-1)M/(n^2 + 2)d$, where M is the molecular weight, and d is the density. If this expression could be extrapolated from the visible region to infinite wave length then it would give approximately the polarization due to the electrons P_e, but would not give the polarization P_a of the atoms, since atoms vibrate with frequencies in the infra red region. Therefore, since P_a is small and extrapolation to infinite wave length only decreases the refraction a small amount, the molar refraction in the visible region can be considered as the electronic contribution to the polarization.

From this it follows that molecular association may have little or no effect upon the value of P_e, and as P_a is small, upon $P_e + P_a$. It is now evident that studies of polarization can be of little aid in the understanding of molecular association if $P_m = 0$. Therefore, it is of interest now to investigate the relation between molecular association and P_m, which according to Debye's (3) theory is equal to $4\pi N\mu^2/9kT$, and where μ is the permanent electric moment of the molecule, k the Boltzmann constant and T the absolute temperature.

The effect of molecular force fields upon one another must depend on the size of their doublets, on the location of the doublets in the molecule, and the geometrical shape of the molecule. Two simple orientations in which two adjacent molecules might be expected to position themsleves in relation to each other are shown in Figure 1. In Figure 1 (a), the negative end of one may attract a positive end of another with the resultant effect of lengthening each separate doublet and giving a moment for both greater than 2μ.

Figure 1

If this occurred, then the number of molecules in the liquid would be cut in half, and N in the expression for P_m would then be N/2, and μ

would be 2μ, so that $P_m = 4\pi(N/2)(2\mu)^2/9kT = 8\pi N\mu^2/9kT$. Therefore, formation of double molecules would double or perhaps more than double P_m since the doublets are lengthened by attraction. It is indeed much too simple a picture, because the extent to which the forces operate is not known. However, even if the two single molecules were not associated definitely to act as one, they would attract one another and orient with respect to each other so that, when a field was applied externally to measure the dielectric constant, the orientation would be greater than that calculated. Also the shape of molecules would prevent an exact lining up of doublets and the axes of each would probably make an angle of less than 180°. As this angle decreases, the polarization decreases and the effect of orientation would be to decrease the polarization instead of increasing it. If the angle between the axes became zero and the doublets were parallel as in Figure 1 (b), the moments would cancel one another and the contribution P_m would become zero. Therefore, this position of the doublets would give a polarization for a polar substance equal to $P_e + P_a$. If the first type of orientation prevails then it is possible for many molecules to be attracted together and a polarization could be built up indefinitely in this manner. Other complex orientations can also be visualized which either increase or decrease the polarization. If there are possibilities of different orientations, it appears probable that if there is not much difference between the energies of the different orientations, one orientation may change to the other as the distances between the dipole molecules change. Therefore, when a polar liquid is dissolved in a nonpolar liquid, the orientation of polar molecules may change from one type to another with change in concentration. When in dilute solution, polar molecules should assume random orientations because they are far apart from one another, unless they form some kind of complex molecule which is not dissociated even in dilute solution. A good example of this is acetic acid in benzene solution. Changes in temperature probably affect the type of orientation. Increasing temperature increases the thermal agitation of molecules and opposes orientation, thereby decreasing the polarization, reducing the abnormalities of liquids, and conformation to the Debye (3) equation becomes closer.

V. PREPARATION OF COMPOUNDS USED

Titaniumtetraethylate - $Ti(OC_2H_5)_4$: This compound has been prepared by Bischoff and Adkins (6) according to the reaction

$$TiCl_4 + 4NaOC_2H_5 \rightarrow Ti(OC_2H_5)_4 + 4NaCl.$$

Crowe (1) describes the reactions and preparations of this compound in detail. The preparation and steps were followed exactly except for one modification. The material contained in the reaction flask, which included NaCl, $Ti(OC_2H_5)_4$, and C_2H_5OH, was refluxed for approximately two to three hours after the reaction. This was found to increase the yield. Analyses for titanium by means of hydrolysis to $Ti(OH)_4$ and ignition to TiO_2, gave a titanium content of 20.89%, 20.87%, 21.04%, 20.89%. The theoretical value is 21.03%.

Titaniumtetrapropylate - $Ti(OC_3H_7)_4$: This compound was prepared by a method similar to that used in the preparation of $Ti(OC_2H_5)_4$. The reaction is

$$TiCl_4 + 4NaOC_3H_7 \rightarrow Ti(OC_3H_7)_4 + 4NaCl$$

and is described in detail in the thesis of Katz (2). Analyses for titanium gave values of 16.77%, 16.82%. The theoretical value is 16.90%.

Titaniumtetrabutylate - $Ti(OC_4H_9)_4$: This compound was prepared in the same manner as $Ti(OC_2H_5)_4$. The reaction is

$$TiCl_4 + 4NaOC_4H_9 \rightarrow Ti(OC_4H_9)_4 + 4NaCl.$$

Analyses for titanium gave values of 13.93%, 14.06%. The theoretical value is 14.08%.

Monochloro-triethoxy-titanium - $TiCl(OC_2H_5)_3$: This compound was prepared previously by Hodgson (8) and Katz (2) and used in the work described herein. It was prepared according to the method described by

Jennings, Wardlow and Way (7) by the reaction

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

The percentage of titanium found was 21.77%. The theoretical value is 21.97%. Chlorine found: 16.37%. Theoretical: 16.22%

VI. POLARIZATION OF $Ti(OC_2H_5)_4$ AT LOW TEMPERATURES

The molar polarization of $Ti(OC_2H_5)_4$ has been determined at temperatures ranging from 17°C to -60°C. By measuring the capacitance of a series of dilute solutions the dielectric constants of solutions may be computed. The densities of these solutions were then measured and with these preliminary data it was possible to calculate the molar polarizations of the compounds.

Apparatus used for measurements: The apparatus used for these determinations is described in Crowe's thesis (1). A pump was connected, through a series of copper coils, to a small thermos reservoir. The reservoir and pump were connected directly to the water jacket of the cell containing the solutions. Technical acetone was pumped through the copper coils which were immersed in a large thermos containing the cooling solution of acetone and dry ice. The acetone cooled in this manner was free of CO_2 and gave a steady flow. The acetone was then introduced into the reservoir, and then forced through the cell. The purpose of the reservoir was to facilitate the filling of the system with acetone.

A chromel-alumel thermocouple was used for the temperature measurement. One junction was kept in a constant temperature bath at 25°C and the other junction was in the solution in the cell. The temperature was taken by reading the emf produced on a D'Arsonval type galvanometer manufactured by the Sensitive Research Corporation. The instrument was a D. C. Polyranger, No. 91362. The voltage range was from 0.005 volt to 1 K.V. The emf was plotted against the temperature and by means of this graph the temperature could be found. The thermocouple was calibrated by using the freezing points of mercury, chloroform, and at temperatures from -10°C to 25°C a bureau of standards mercury thermometer was employed.

The cell used for these measurements in the beginning was the same one employed by Crowe (1) in his determinations, but some difficulties, such as leakage of the water jacket, developed in its use and a new one was constructed which was essentially the same except that it was entirely of glass construction. Copper foil was wrapped around the outside of the cell and used for ground. This deteriorated and had to be replaced but caused very little change in the cell constant, as Table I indicates. Copper foil was replaced after Trial number 1 and 2. These values were all taken at 25°C.

TABLE I

Trial No.	C_a	C_x	C
1	32.40	63.76	24.64
2	32.55	63.83	24.58
3	32.62	63.97	24.64

C_x is the capacitance of the cell with benzene, C_a is the capacitance of the cell with air, and C is the cell constant.

To check the cell constant, the dielectric constant of n-hexane was determined at 25°C. These values are shown in Table II. Heil's value for a petroleum fraction of hexane is 1.885 (9).

TABLE II

Trial No.	C_a	C_x	C	
1	32.40	63.76	24.64	1.8819
2	32.55	63.83	24.58	1.8841
3	32.62	63.97	24.64	1.8813

The method used to calculate these polarizations is described in Crowe's and Katz' theses (1) (2).

Polarization of $Ti(OC_2H_5)_4$ from 20°C to -60°C.

In order to determine the variation of the cell constant with temperature in the range from 20°C to -60°C, it was found necessary to determine a cell constant in the temperature range from 10°C to 20°C. (See Table VI). This was accomplished by measuring the capacitance of air, benzene and hexane and these temperatures. (See Fig.'s 3, 4, 5). From these data the dielectric constant of n-hexane was calculated at these temperatures and then extrapolated. (Table VII, Fig. 6). By using the extrapolated values of the dielectric constant of n-hexane, the dielectric constant of air, and the capacitance of the cell with n-hexane and air in the lower temperature region, a cell constant was calculated for the range from 0°C to -50°C. (See Table VIII, Fig 7) Heil's values (9) for the variation of the dielectric constant of n-hexane with temperature (Table VII) were also plotted in Figure 6 for purposes of comparison. The values that had been obtained previously (See Table II) for the dielectric constant of n-Hexane at 25°C are also plotted and indicate fairly good results in the extrapolation. The hexane that Heil (9) used for the determinations was a petroleum fraction and therefore the values are different, probably due to the various other components which contributed to the capacitance.

Several accurately weighed dilute solutions of $Ti(OC_2H_5)_4$ were made up using pure n-hexane as the solvent. The n-hexane used was Phillips 66 pure grade n-hexane. It was stored over P_2O_5 and redistilled immediately before use to insure the absence of water. The capacitances of the solutions were measured as soon as they were made up to minimize any error that could possibly be introduced due to absorption of water vapor. (See Table IX, Fig. 8). Densities of solutions were measured in the working temperature range by a modified Ostwald pycnometer and a volume correction was applied. Table X shows the results of these measurements.

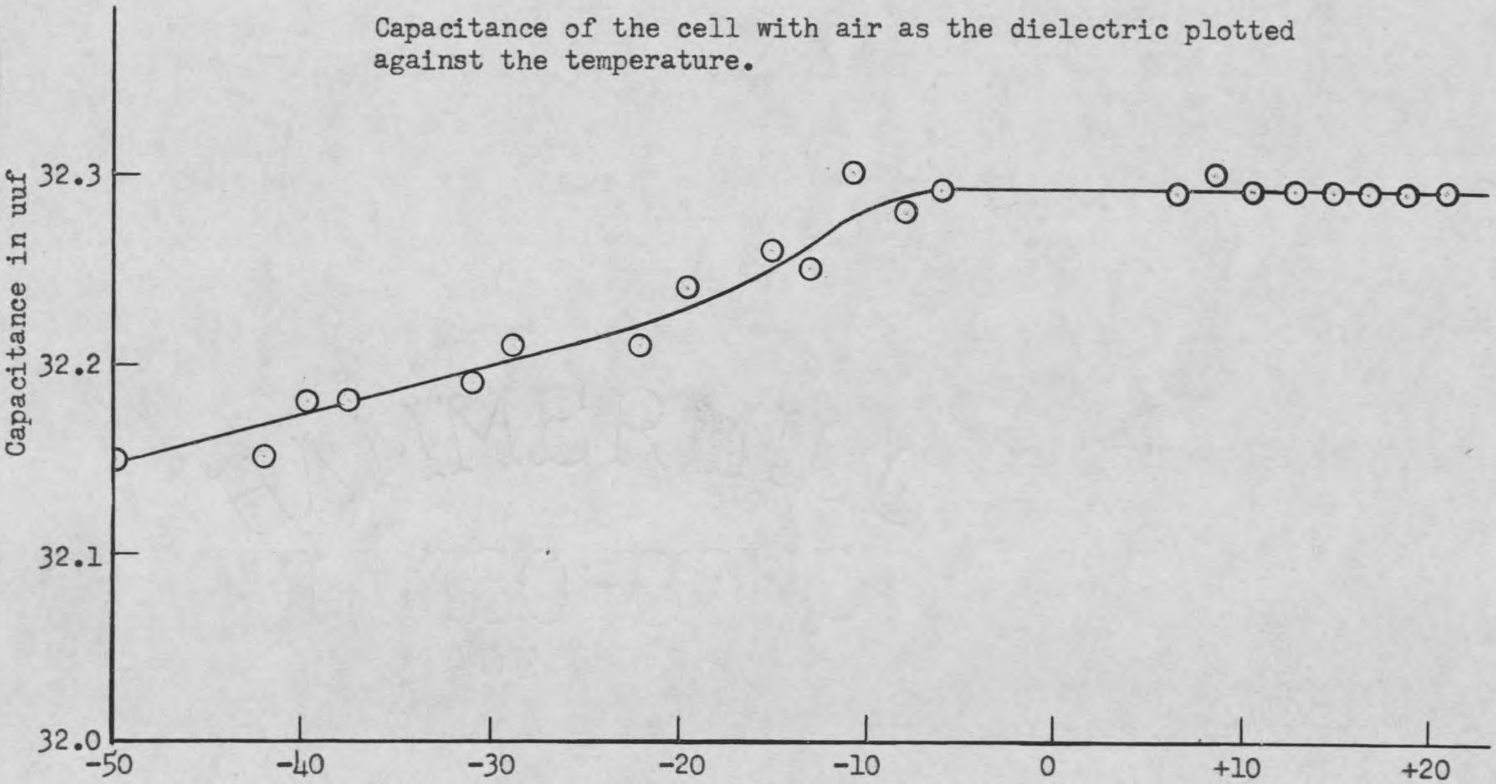
The values of the dielectric constant and specific volumes of solutions were plotted against mole fraction $Ti(OC_2H_5)_4$. Since these were straight lines, Halverstadt's and Kumler's method (10) could be applied in order to determine the slopes and intercepts of these lines. Figure 10 and Figure 11 show that these lines are linear. The values obtained for the slopes and intercepts are shown in Table XIII. α and β are the slopes of the dielectric constant and specific volume lines respectively, and ϵ_1 and V_1 are the intercepts, or the dielectric constant and specific volume of the pure solvent. These values were then inserted into Halverstadt's and Kumler's equation for the polarization at infinite dilution. The values obtained are shown in Table XIV. (See Fig. 12).

In Figures 2 and 3, all the values were not plotted since some points were very near or coincided with other points on the graph.

TABLE III

Capacitance of cell with air at various temperatures
(Temperature in Centigrade, Capacitance in $\mu\mu f$)

T	C_a	T	C_a	T	C_a
-49.9	32.15	-15.2	32.26	+10.6	32.29
-42.0	32.15	-13.0	32.25	+12.7	32.29
-39.9	32.18	-10.8	32.30	+14.7	32.29
-37.7	32.18	-8.1	32.28	+16.8	32.29
-30.9	32.19	-6.3	32.29	+18.8	32.29
-28.8	32.21	+4.5	32.26	+20.9	32.29
-22.1	32.21	+6.6	32.29		
-19.8	32.24	+8.6	32.30		



Capacitance of the cell with air as the dielectric plotted against the temperature.

Figure 2

TABLE IV

Capacitance of cell with n-hexane at various temperatures.
(Temperature in Centigrade, Capacitance in)

T	C_h	T	C_h	T	C_h
-57.8	56.92	-24.3	55.75	+10.6	54.55
-55.2	56.83	-22.1	55.68	+12.7	54.48
-51.2	56.68	-19.8	55.61	+14.7	54.40
-48.6	56.58	-17.5	55.51	+16.8	54.33
-46.7	56.51	-13.0	55.39	+18.8	54.25
-42.0	56.34	- 8.5	55.25	+20.9	54.20
-37.7	56.19	+ 4.9	54.76	+21.7	54.15
-33.2	56.04	+ 6.6	54.69	+22.9	54.11
-28.3	55.88	+ 8.6	54.62		

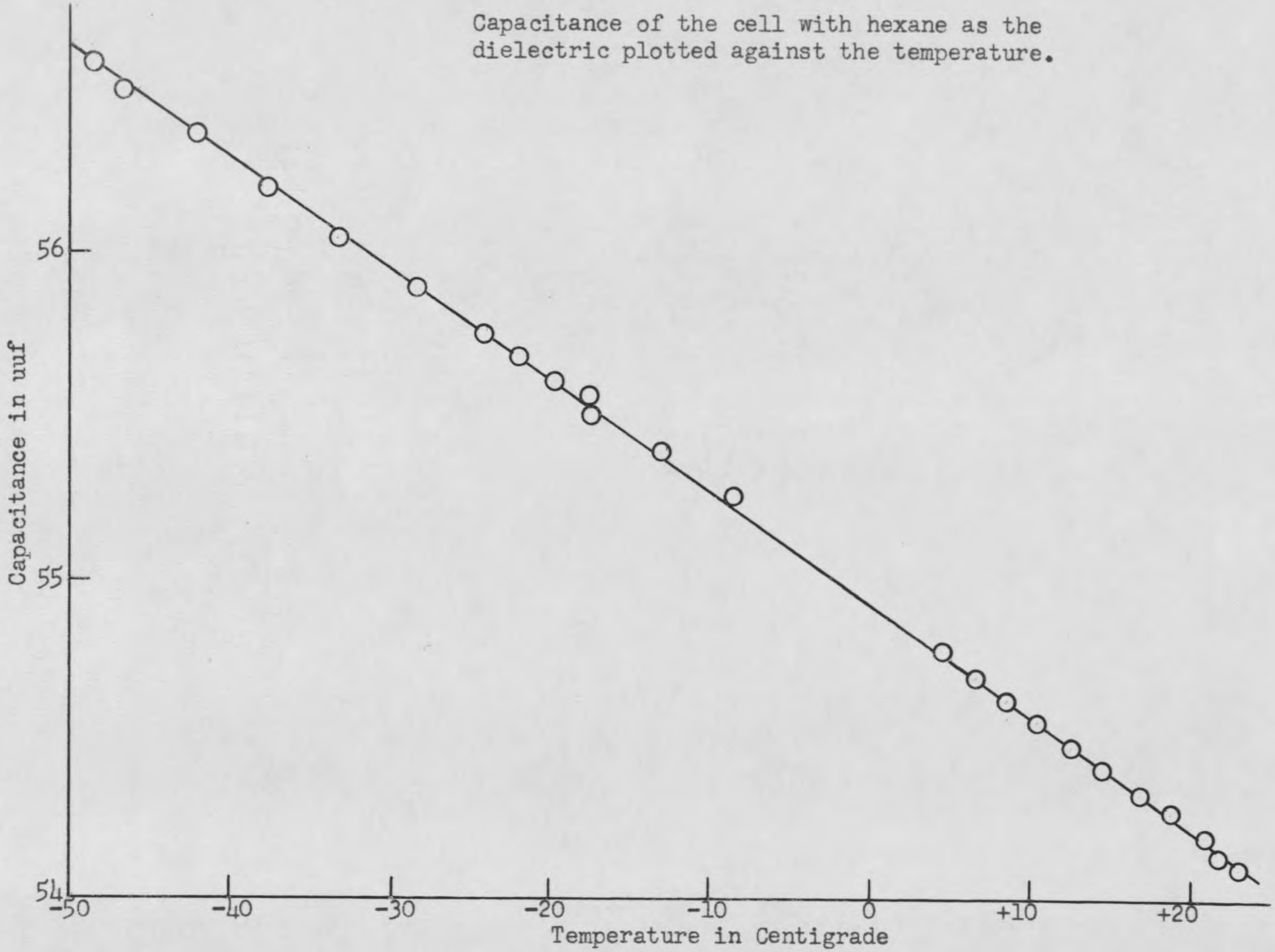

Capacitance of the cell with hexane as the
dielectric plotted against the temperature.
Capacitance in uuf
56
55
54
-50
-40
-30
-20
-10
0
+10
+20
Temperature in Centigrade

Figure 3

TABLE V

Capacitance of cell with benzene at various temperatures
(Temperature in Centigrade, Capacitance in $\mu\mu f$)

T	C_b	T	C_b
+8.6	64.52	+8.6	64.46
+10.6	64.38	+10.6	64.37
+12.7	64.29	+12.7	64.25
+14.7	64.18	+14.7	64.13
+16.8	64.07	+16.8	64.05
+18.8	63.98	+18.8	63.93
+20.9	63.88	+20.9	63.83

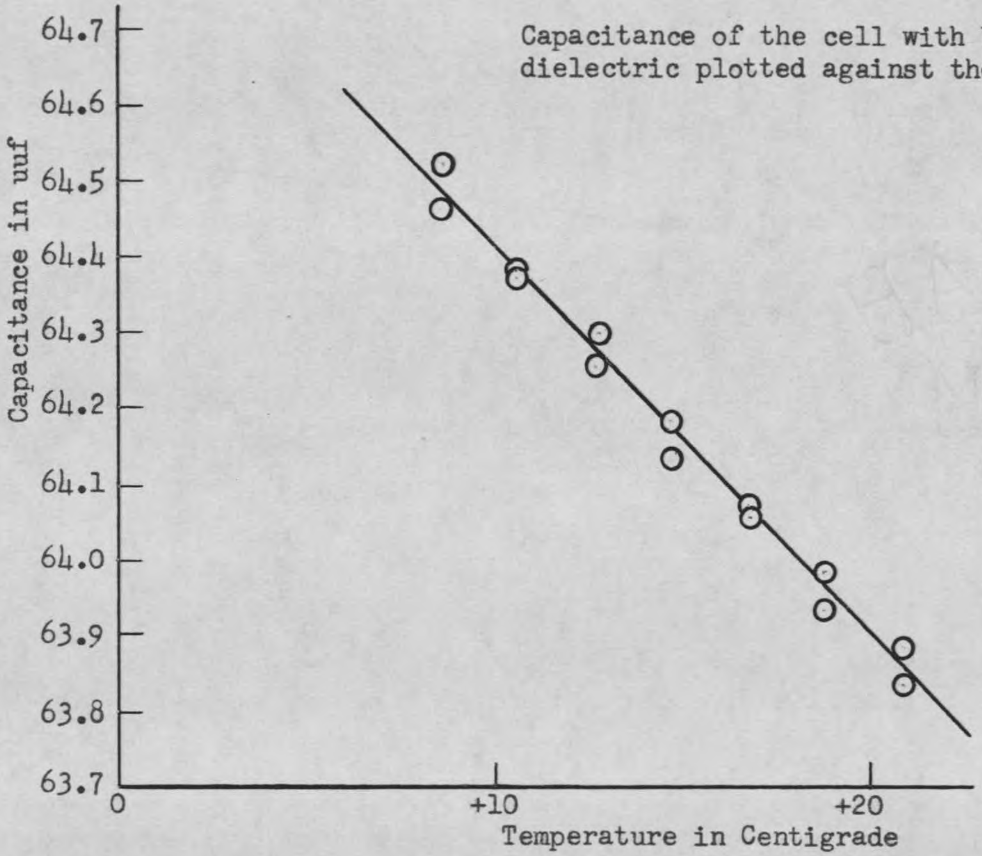


Figure 4

Capacitance of the cell with benzene as the dielectric plotted against the temperature.

TABLE VI

Variation of cell constant with temperature
(Temperature in Centigrade)

T	C
+10	24.66
+15	24.64
+20	24.63

TABLE VII

Variation of dielectric constant

of n-hexane with temperature
(Temperature in Centigrade)

T	
+10	1.9030
+15	1.8966
+20	1.8900

Hiel's values of variation of dielectric

constant of n-hexane with temperature
(Temperature in Centigrade)

T	
-60	2.0100
-50	1.9950
-40	1.9800
-30	1.9660
-20	1.9520
-10	1.9370
0	1.9230
+10	1.9080
+20	1.8930

Figure 5

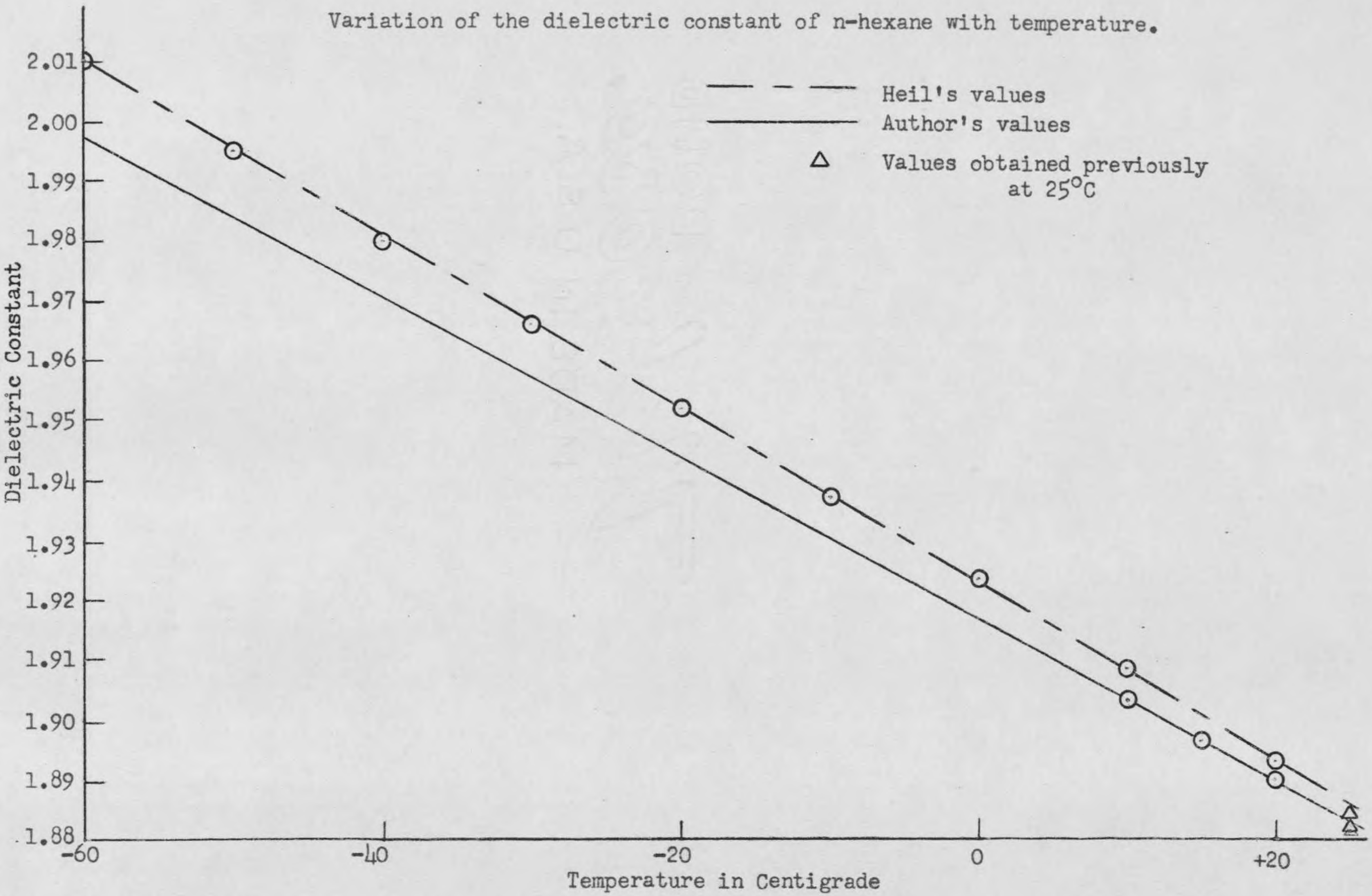

Variation of the dielectric constant of n-hexane with temperature.
Heil's values
Author's values
Values obtained previously at 25°C
Dielectric Constant
2.01
2.00
1.99
1.98
1.97
1.96
1.95
1.94
1.93
1.92
1.91
1.90
1.89
1.88
-60
-40
-20
0
+20
Temperature in Centigrade

TABLE VIII

Variation of cell constant with temperature
(Temperature in Centigrade)

T	C
-50	24.95
-40	24.90
-30	24.86
-20	24.82
-10	24.74
0	24.69
+10	24.66
+20	24.63

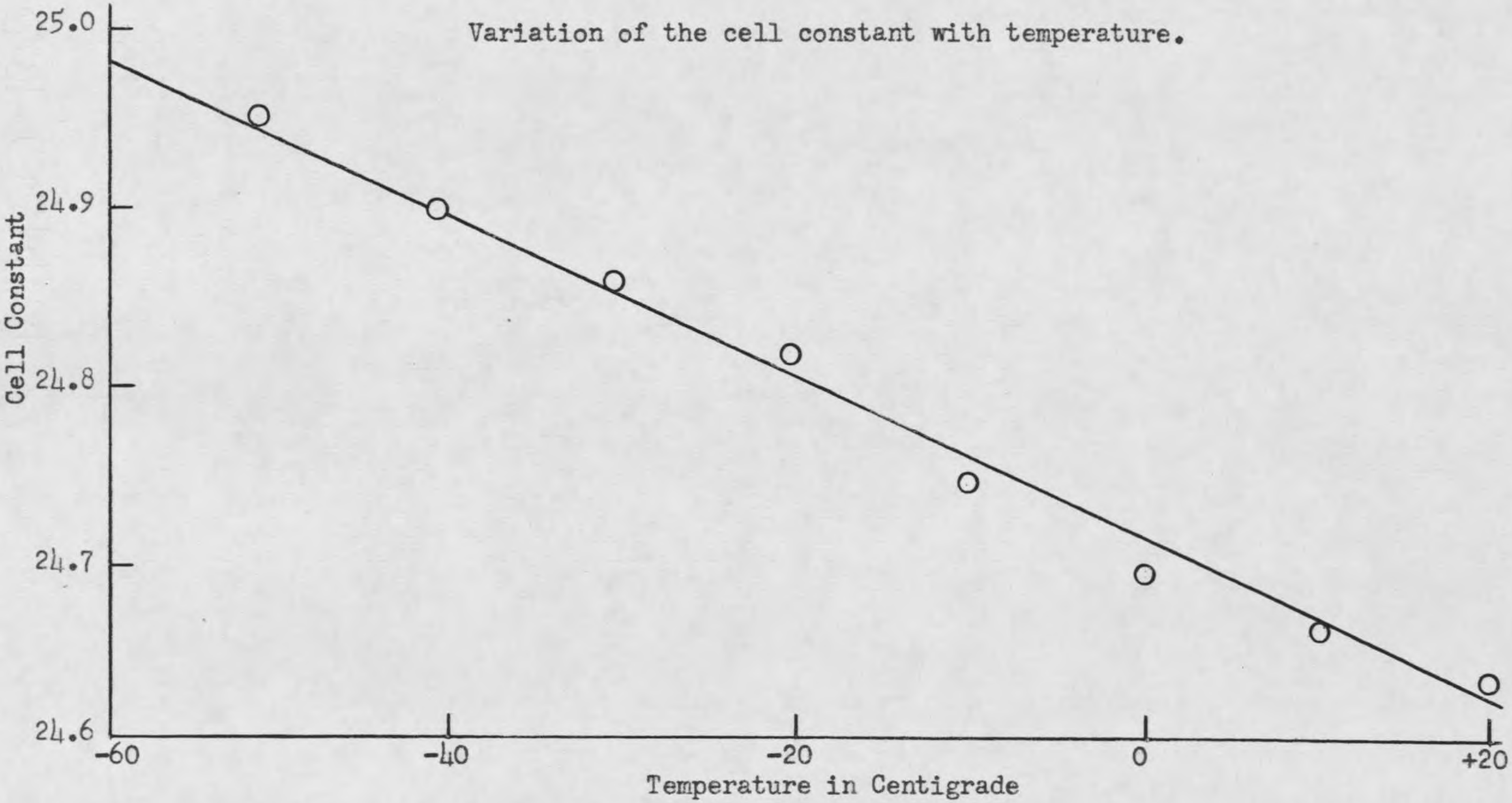

Variation of the cell constant with temperature.
Cell Constant
25.0
24.9
24.8
24.7
24.6
-60
-40
-20
0
+20
Temperature in Centigrade

Figure 6

TABLE IX

Capacitance of solutions at various temperatures
(Temperature in Centigrade, Capacitance in $\mu\mu f$)

T	Solution number 1	Solution number 2	Solution number 3	Solution number 4	Solution number 5
-57.8	57.24	57.52	57.66	57.80	58.08
-53.4	57.06	57.30	57.44	57.57	57.86
-49.0	56.89	57.15		57.41	57.66
-44.4	56.70	56.96	57.08	57.24	57.51
-39.9	56.53	56.79	56.91	57.11	57.33
-35.4	56.39	56.61	56.75	56.97	57.17
-30.9	56.22	56.48	56.59	56.82	56.99
-26.5	56.07	56.30	56.43	56.69	56.80
-22.1	55.93	56.14	56.28	56.54	56.69
-17.5	55.76	55.97	56.14	56.40	56.54
-13.0	55.63	55.86	55.99	56.25	56.38
-8.5	55.49	55.71	55.84	56.10	56.23
+4.5		55.20	55.34	55.56	55.68
+8.6	54.80	55.05	55.16	55.41	55.54
+12.7	54.64	54.91	55.01	55.27	55.38
+16.8	54.50	54.76	54.85	55.11	55.25
+18.8		54.67			

Capacitance of the solutions plotted against the temperature

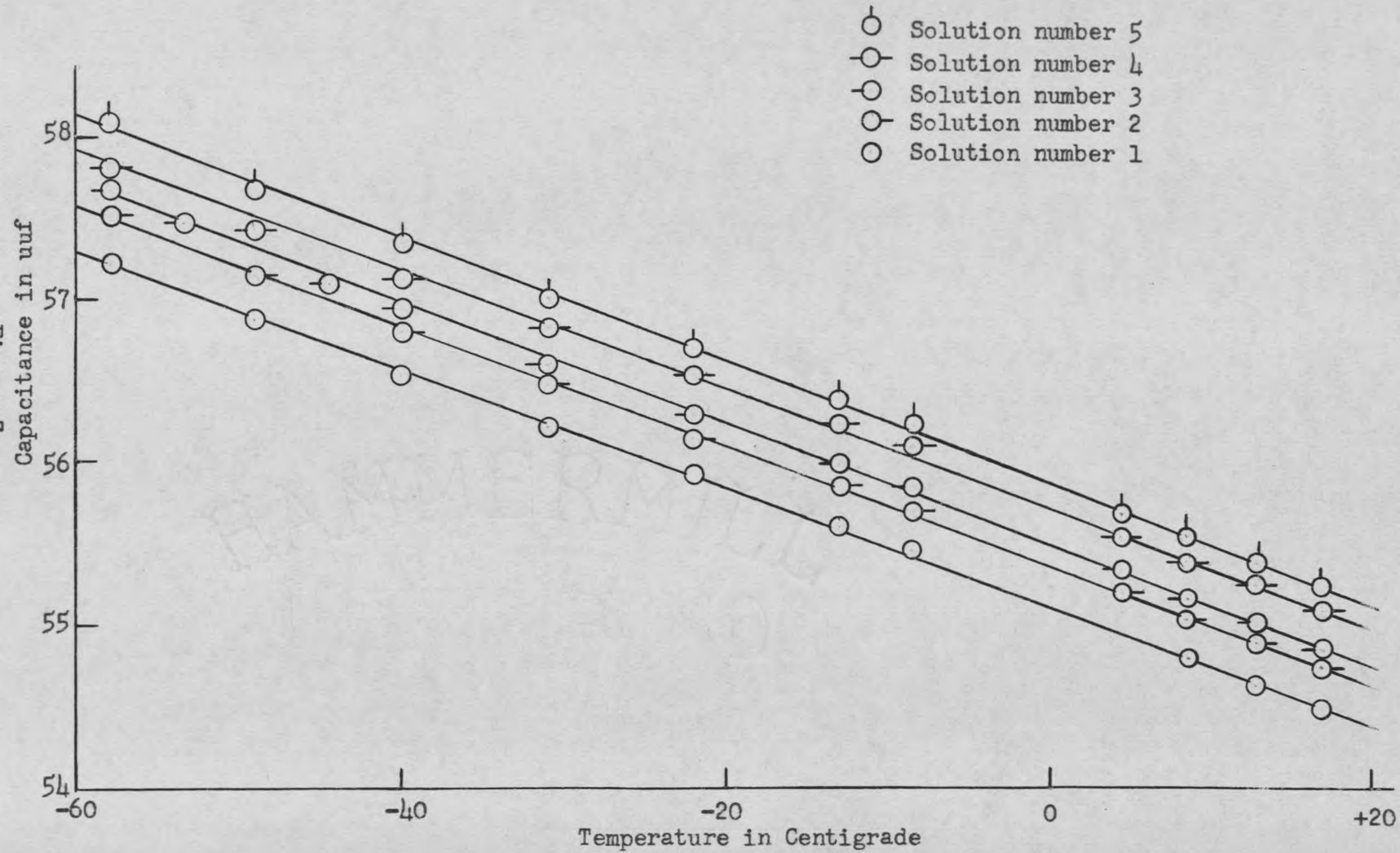


Figure 7

TABLE X

Specific volumes of solutions at various temperatures
(Temperature in Centigrade)

T	Solution number 1	Solution number 2	Solution number 3	Solution number 4	Solution number 5
-60	1.3711	1.3664	1.3640	1.3622	1.3557
-50	1.3873	1.3823	1.3800	1.3781	1.3715
-40	1.4037	1.3986	1.3962	1.3943	1.3875
-30	1.4206	1.4154	1.4130	1.4110	1.4041
-20	1.4376	1.4324	1.4300	1.4279	1.4208
-10	1.4553	1.4499	1.4473	1.4452	1.4380
0	1.4734	1.4680	1.4652	1.4632	1.4556
+10	1.4918	1.4863	1.4836	1.4814	1.4736
+17	1.5051	1.4994	1.4967	1.4945	1.4865

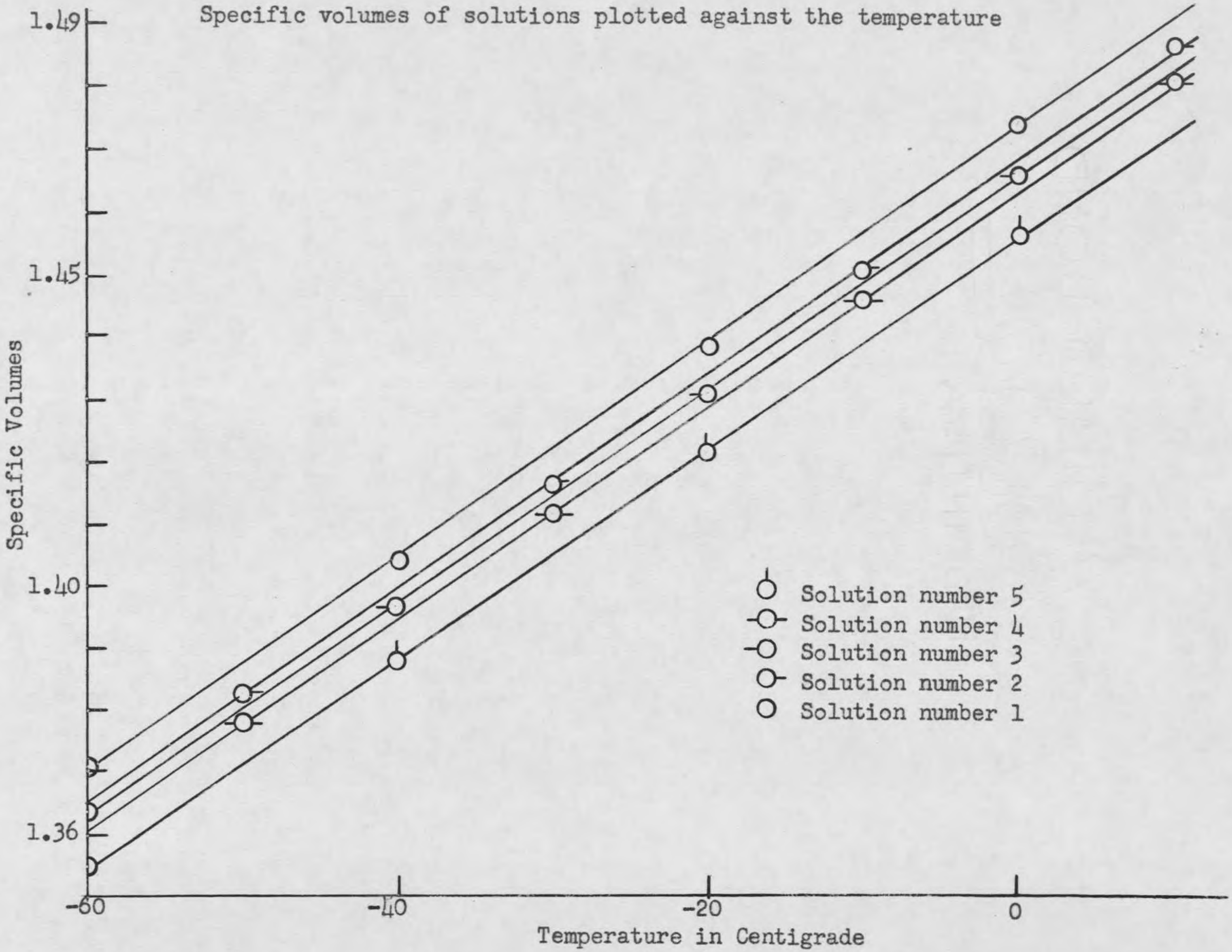

Specific volumes of solutions plotted against the temperature
1.49
1.45
1.40
1.36
Specific Volumes
-60
-40
-20
0
Temperature in Centigrade
Solution number 5
Solution number 4
Solution number 3
Solution number 2
Solution number 1

Figure 8

TABLE XI

Dielectric constants of solutions versus mole fraction of $Ti(OC_2H_5)_4$

Solution number =	1	2	3	4	5
Mole fraction $Ti(OC_2H_5)_4$ =	0.002909	0.006676	0.008852	0.010343	0.014726
-60°C	2.0071	2.0169	2.0225	2.0302	2.0395
-50	1.9934	2.0031	2.0086	2.0166	2.0252
-40	1.9795	1.9892	1.9945	2.0029	2.0110
-30	1.9657	1.9754	1.9806	1.9892	1.9968
-20	1.9519	1.9616	1.9667	1.9754	1.9826
-10	1.9381	1.9479	1.9528	1.9618	1.9684
0	1.9244	1.9341	1.9389	1.9481	1.9544
+10	1.9106	1.9204	1.9250	1.9345	1.9402
+17	1.9009	1.9107	1.9153	1.9250	1.9304

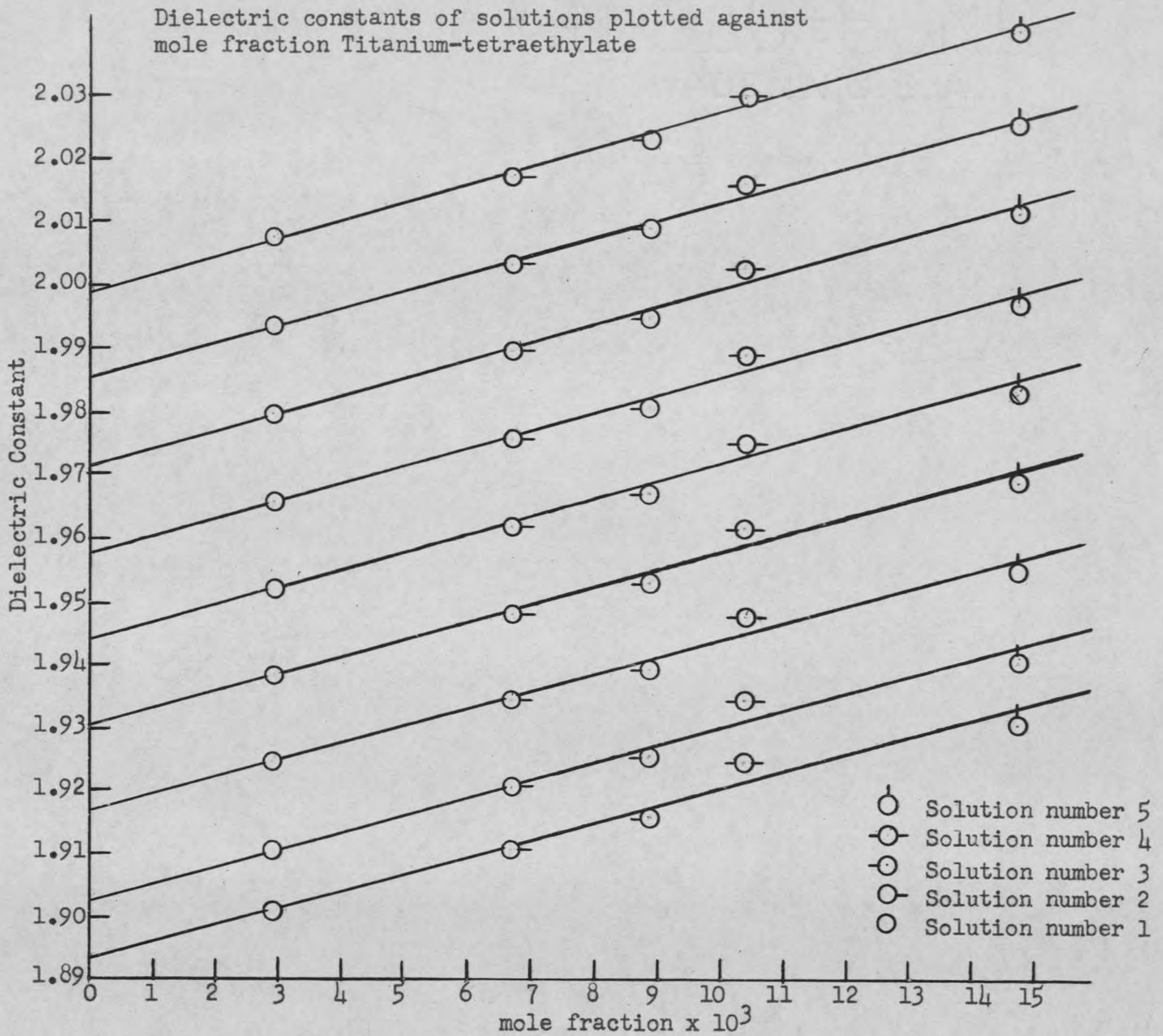

Dielectric constants of solutions plotted against
mole fraction Titanium-tetraethylate
Dielectric Constant
2.03
2.02
2.01
2.00
1.99
1.98
1.97
1.96
1.95
1.94
1.93
1.92
1.91
1.90
1.89
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
mole fraction x 10^3
Solution number 5
Solution number 4
Solution number 3
Solution number 2
Solution number 1

Figure 9

TABLE XII

Specific volumes of solutions versus mole fraction of $Ti(OC_2H_5)_4$

Solution number =	1	2	3	4	5
Mole fraction $Ti(OC_2H_5)_4$ =	0.003176	0.006676	0.008852	0.010343	0.014726
-60°C	1.3711	1.3664	1.3640	1.3622	1.3557
-50	1.3873	1.3823	1.3800	1.3781	1.3715
-40	1.4037	1.3986	1.3962	1.3943	1.3875
-30	1.4206	1.4154	1.4130	1.4110	1.4041
-20	1.4376	1.4324	1.4300	1.4279	1.4208
-10	1.4553	1.4499	1.4473	1.4452	1.4380
0	1.4734	1.4680	1.4652	1.4632	1.4556
+10	1.4918	1.4863	1.4836	1.4814	1.4736
+17	1.5051	1.4994	1.4967	1.4945	1.4865

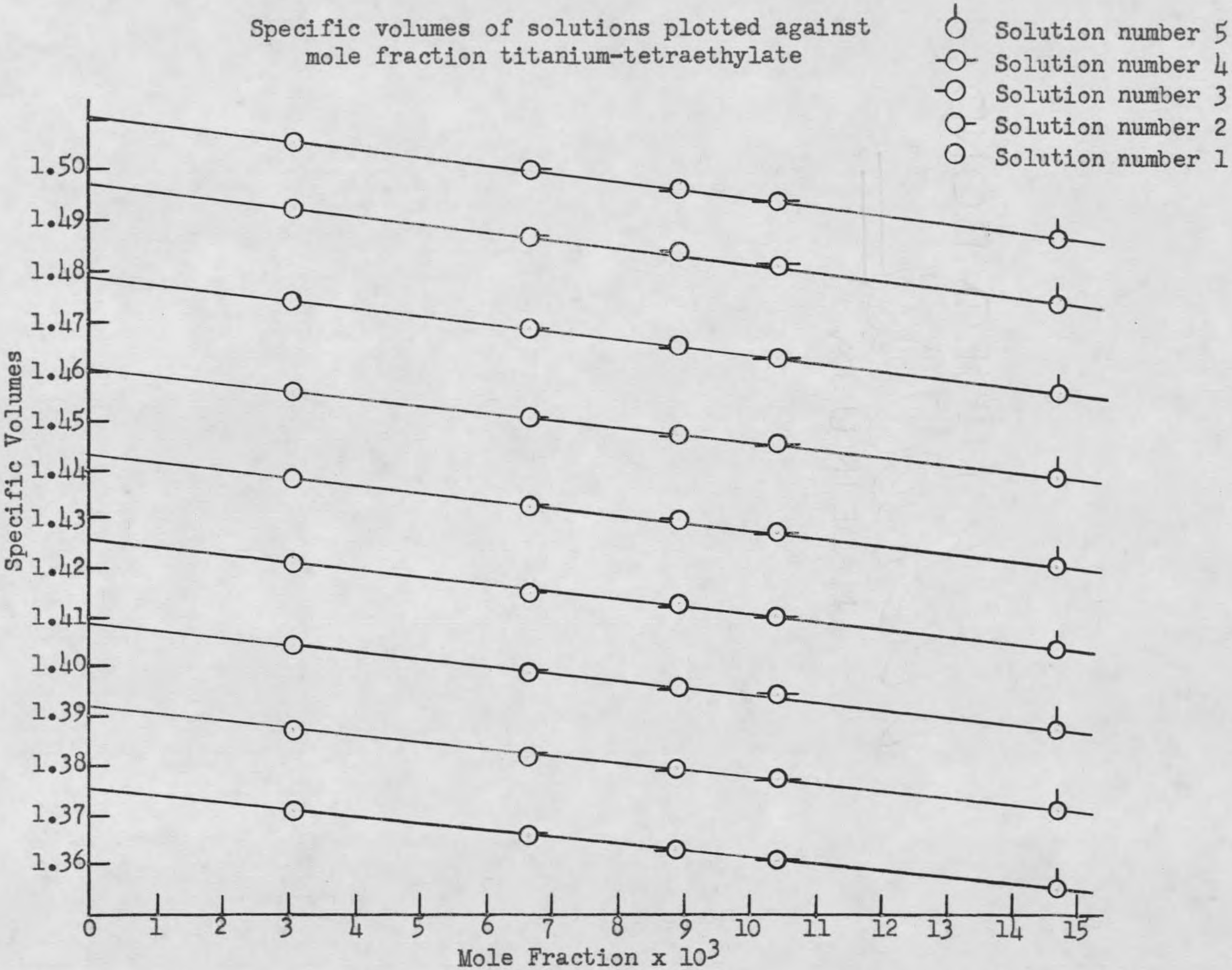

Specific volumes of solutions plotted against
mole fraction titanium-tetraethylate
Solution number 5
Solution number 4
Solution number 3
Solution number 2
Solution number 1
Specific Volumes
1.50
1.49
1.48
1.47
1.46
1.45
1.44
1.43
1.42
1.41
1.40
1.39
1.38
1.37
1.36
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Mole Fraction x 10^3

Figure 10

TABLE XIII

Slopes and Intercepts

T °C		v_1		
-60	1.99880	1.37554	2.80850	-1.32614
-50	1.98531	1.39171	2.76536	-1.34962
-40	1.97151	1.40817	2.74767	-1.38116
-30	1.95789	1.42524	2.71719	-1.41628
-20	1.94427	1.44233	2.68502	-1.43379
-10	1.93068	1.46019	2.65663	-1.48439
0	1.91706	1.47841	2.63384	-1.52189
+10	1.90345	1.49705	2.60675	-1.56038
+17	1.89383	1.51039	2.60073	-1.58806

TABLE XIV

Polarization at infinite dilution of $Ti(OC_2H_5)_4$

versus 1/absolute temperature

$1/T \times 10^3$	Polarization
4.69	112.29
4.48	112.38
4.28	112.88
4.11	113.06
3.94	113.55
3.79	113.49
3.66	113.86
3.53	114.12
3.44	114.64

Polarization at infinite dilution of
$Ti(OC_2H_5)_4$ plotted against 1/T

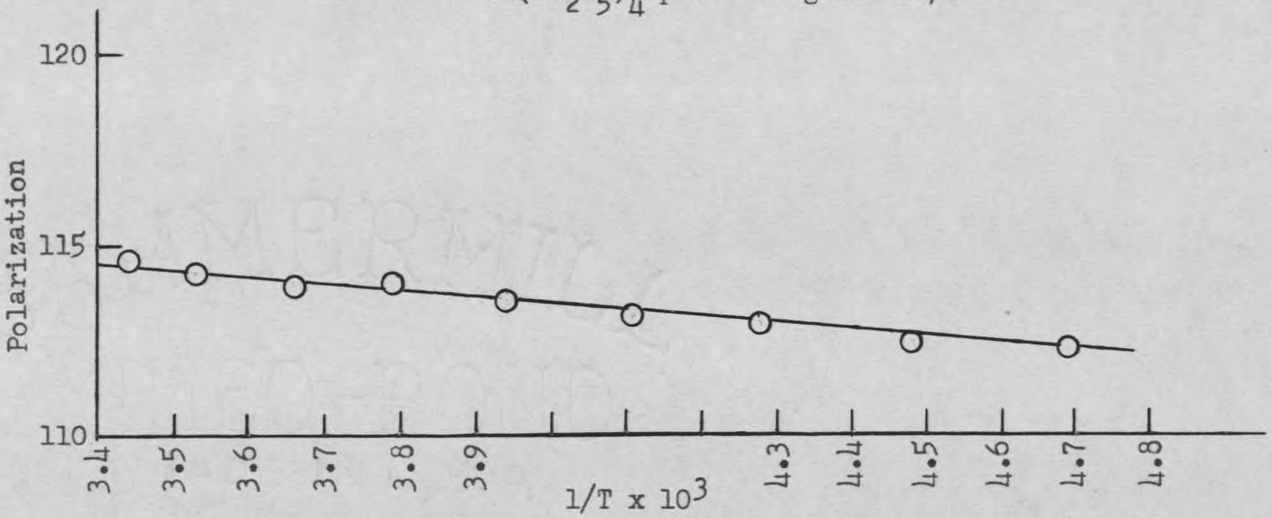


Figure 12

VII. DEGREES OF ASSOCIATION

A study has been made of the degrees of association of propyl and butyl ortho-titanates and monochloro-triethoxy-titanium in benzene solution. The benzene used for the determinations was Mercks C.P. benzene, thiophene free. The benzene was kept over sodium and then distilled immediately before use. Thoroughly dried glass stoppered flasks were used in making up the solutions. The solutions were then used immediately for the determinations. Fairly good results could be obtained for the propyl and butyl ortho-titantes; however, good results could not be obtained for the monochloro-triethoxy-titanium. Better results were finally obtained by distilling both solute and solvent directly into the apparatus used for the determinations. Both solute and solvent were weighed immediately after collection without access to water vapor in the air. The Beckman freezing point lowering method was used in all cases. In order to facilitate the placing of the Beckman thermometer and stirrer in the receivers, a dry box was used in which phosphorous pentoxide and sulfuric acid reduced the moisture content to a minimum. Neoprene stoppers and tubes were used around the thermometer and stirrer in order to prevent water vapor from entering the apparatus and contamination of the benzene.

In all cases the association factor was approximately 3. The results are indicated in Figures 12, 13, 14, in which association number is plotted against mole fraction solute. Figure 15 indicates the effect of small amounts of water upon the association of mono-chloro-triethoxy-titanium. The addition of water was accomplished by adding drops of benzene saturated with water. The amount of water added can only be considered approximate since it was calculated from the solubility of water in benzene. 0.057 gr./100 gr. benzene. 7.6×10^{-6} gr. water/drop.

TABLE XV

Association of $Ti(OC_3H_7)_4$

Mole fraction	Molecular weight	Association number
0.00204	278	0.978
0.00904	690	2.427
0.01334	831	2.923
0.01773	802	2.821
0.02150	792	2.786
0.02855	764	2.687
0.03790	708	2.490

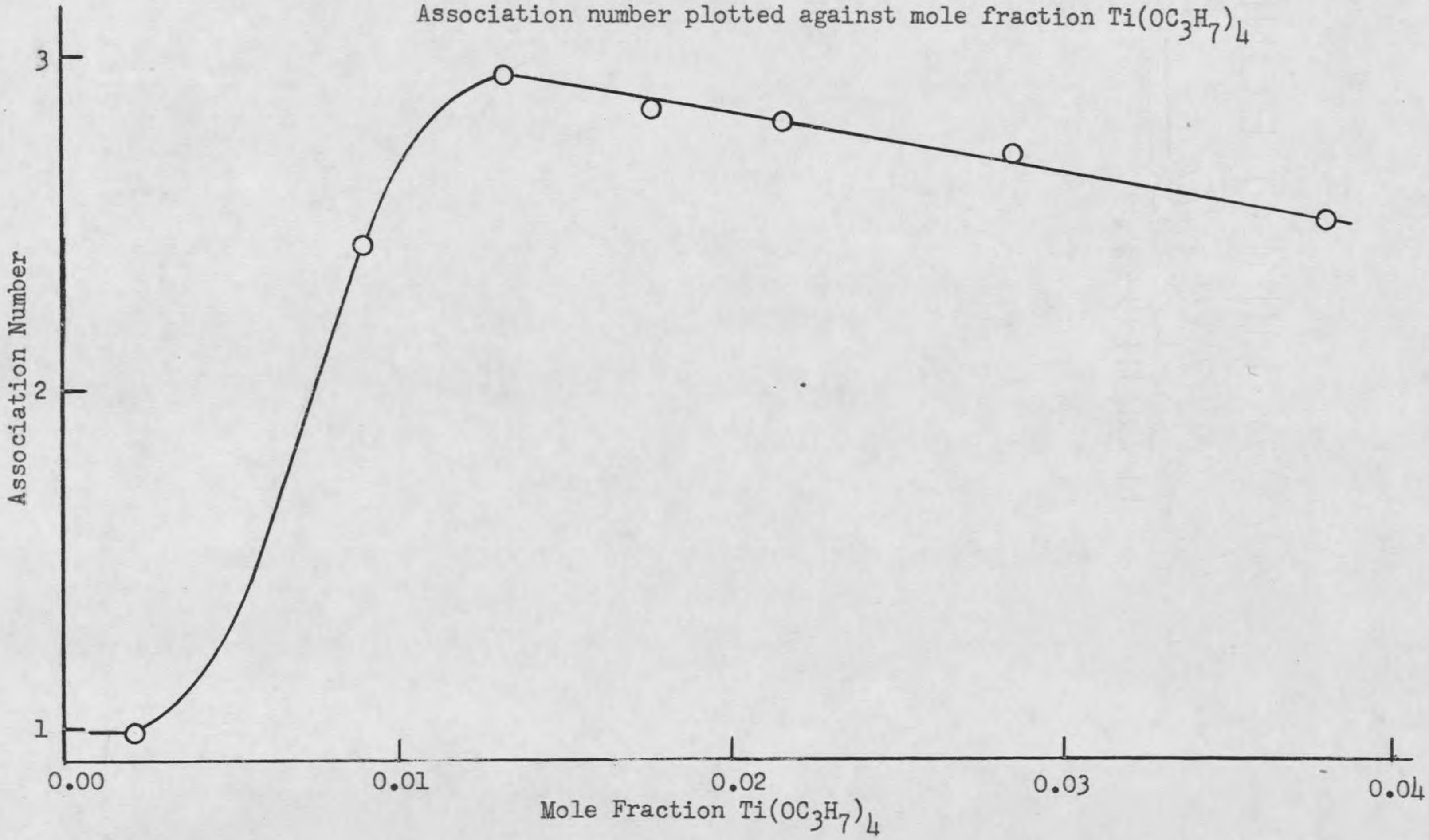

Association number plotted against mole fraction $Ti(OC_3H_7)_4$
Association Number
3
2
1
0.00
0.01
0.02
0.03
0.04
Mole Fraction $Ti(OC_3H_7)_4$

Figure 12

TABLE XVI

Association of $Ti(OC_4H_9)_4$

Mole fraction	Molecular weight	Association number
0.002975	341	1.002
0.004790	440	1.295
0.008670	1024	3.010
0.011680	1033	3.037
0.021990	986	2.897
0.022600	965	2.835

Association number plotted against mole fraction $Ti(OC_4H_9)_4$

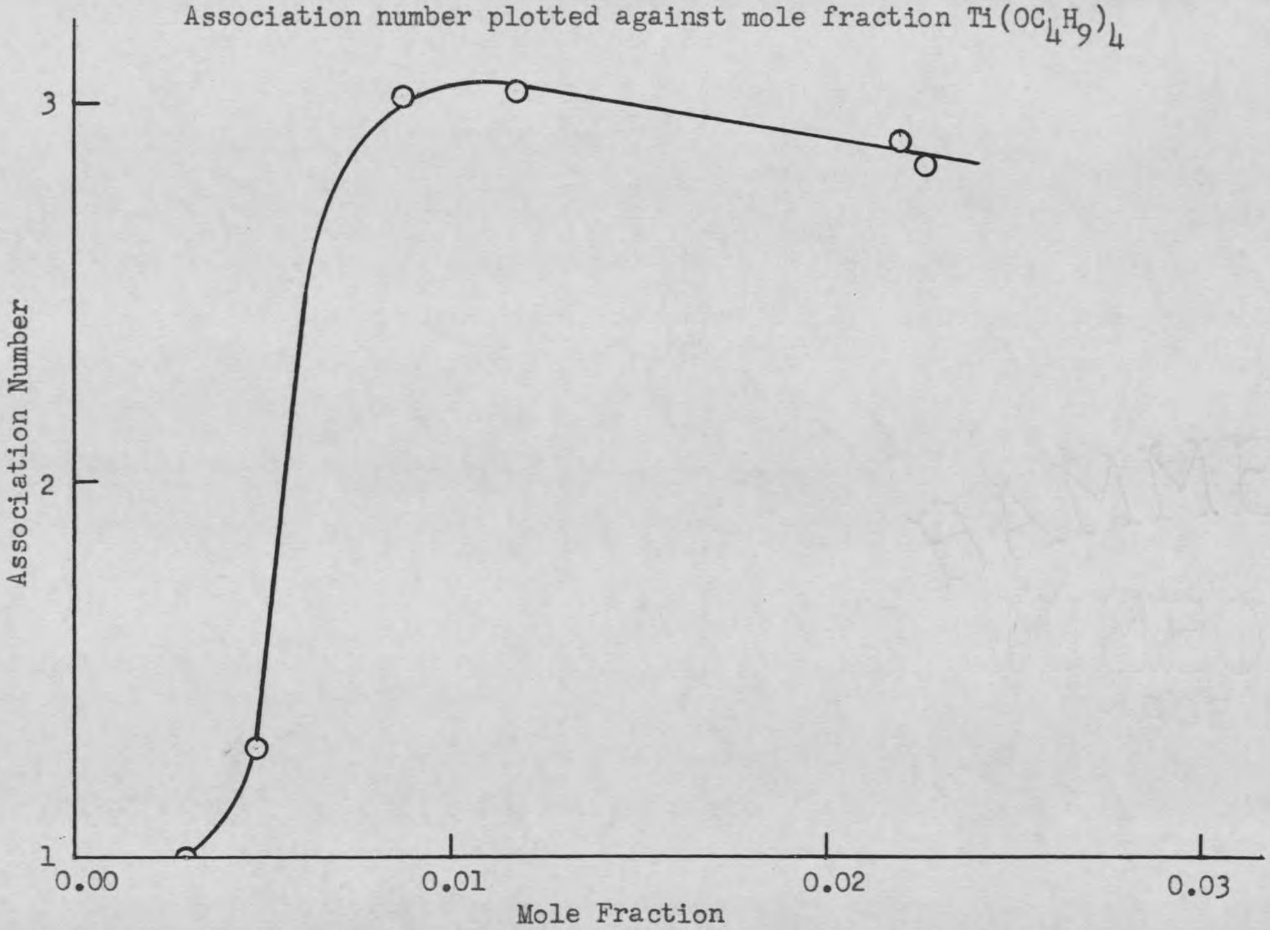


Figure 13

TABLE XVII

Association of $TiCl(OC_2H_5)_3$

Mole fraction	Molecular weight	Association number
First run		
0.004224	467	2.136
0.007396	667	3.052
0.014147	642	2.937
Second run		
0.00646	352	1.610
0.00895	542	2.480
0.01140	639	2.923
Third run		
0.00495	509	2.329
0.00816	677	3.097
0.01174	558	2.553
Fourth run		
0.004782	492	2.251
0.007904	627	2.869
0.010596	667	3.052

Association number plotted against mole fraction $TiCl(OC_2H_5)_3$

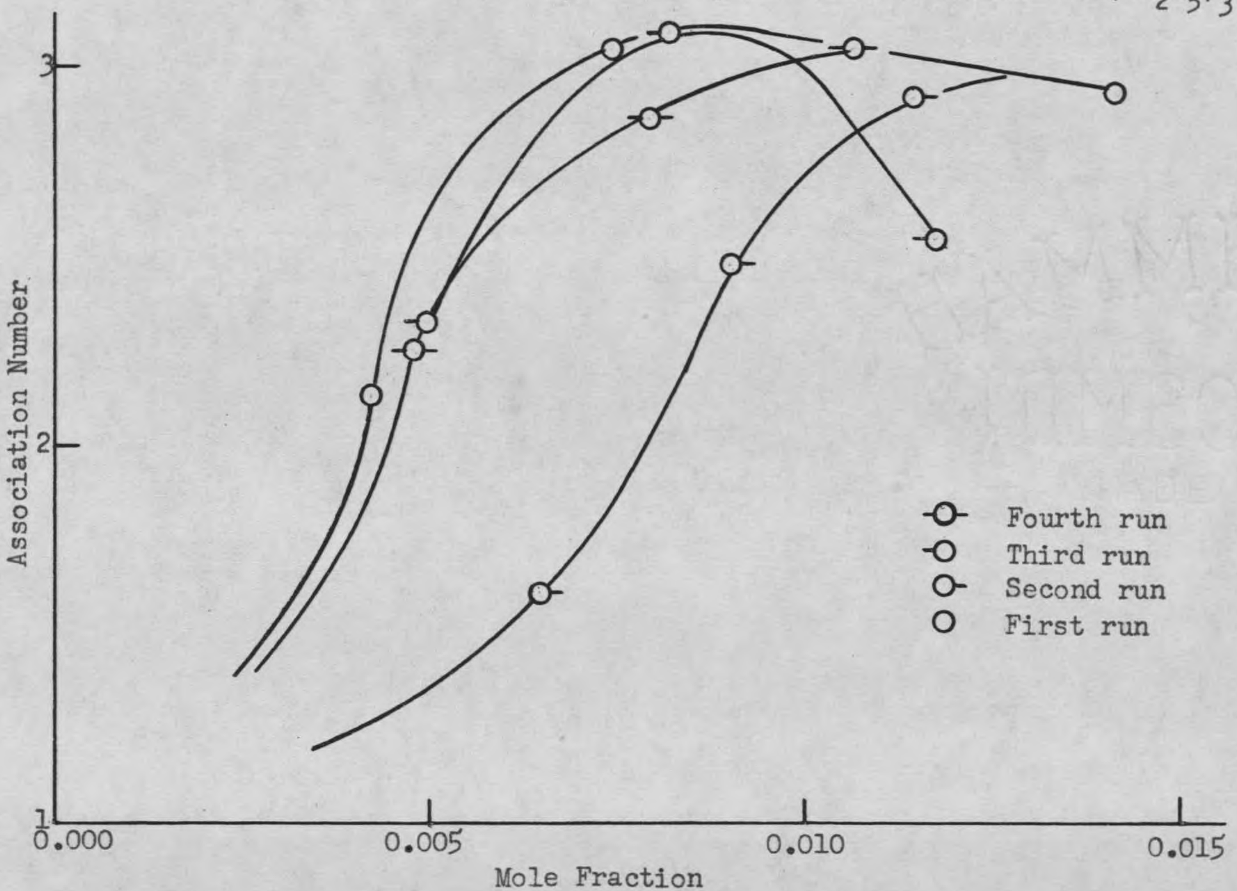


Figure 14

TABLE XVIII

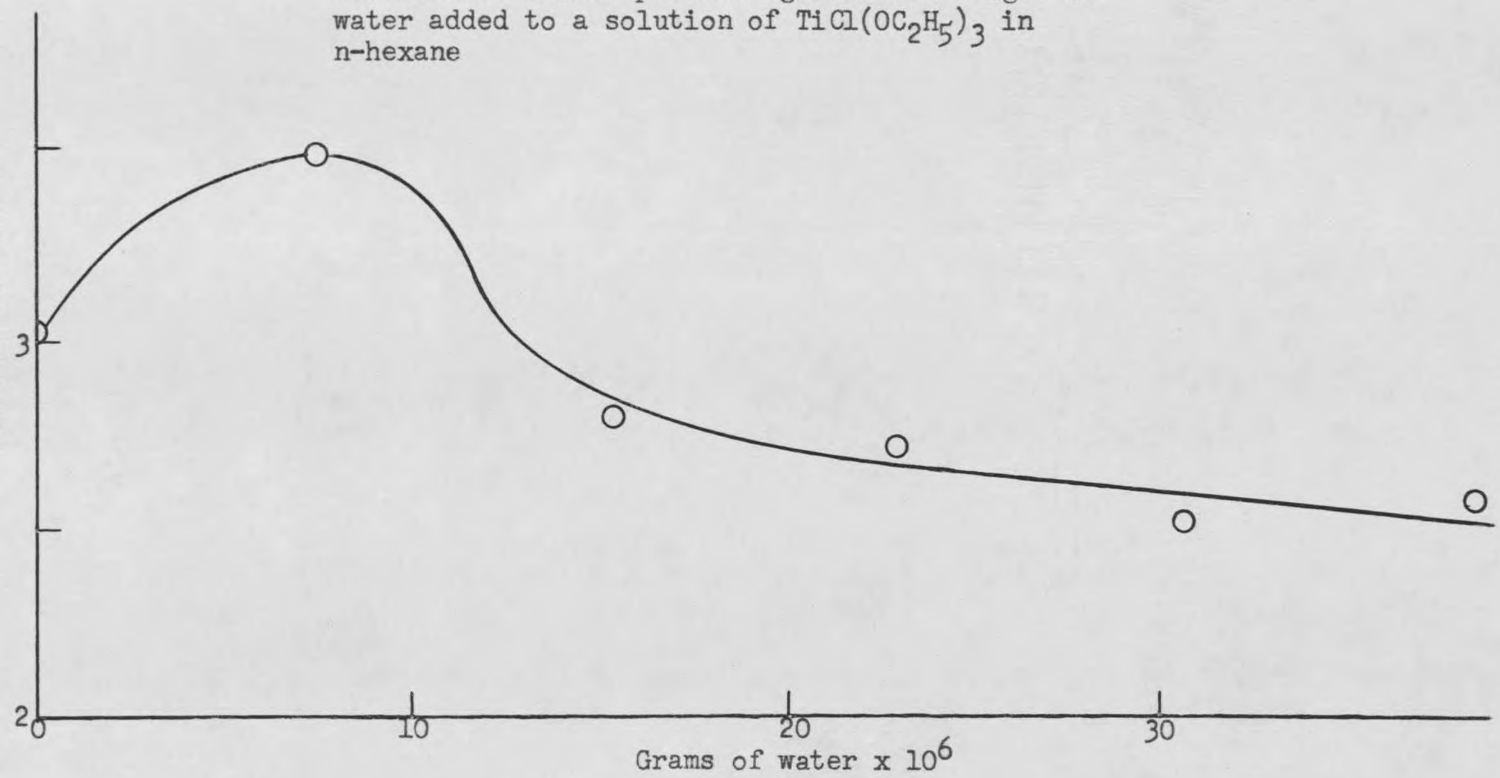
Effect of water on association of $TiCl(OC_2H_5)_3$

Original concentration $TiCl(OC_2H_5)_4$ = 0.007396
Apparent molecular weight = 667
Original association number - 3.052

Weight of water added in grams	Molecular weight	Association number
7.638×10^{-6}	762	3.486
15.276×10^{-6}	610	2.791
22.914×10^{-6}	593	2.713
30.552×10^{-6}	547	2.502
38.190×10^{-6}	562	2.571

Figure 15

Association number plotted against the weight of water added to a solution of $TiCl(OC_2H_5)_3$ in n-hexane



VIII. PREPARATION OF CRYSTALS OF $Ti(OC_2H_5)_4$

Pure crystals of $Ti(OC_2H_5)_4$ were prepared by distilling liquid $Ti(OC_2H_5)_4$ into a series of small (6 mm i.d.) glass tubes at a pressure of 1-2 mm. The tubes contained a fine glass wire running through the center and sealed at one end of the tube. Each of the tubes was filled approximately one-third full, and sealed off under vacuum. They were allowed to stand for a period of two to six weeks and at the end of two weeks, very small crystals could be detected on the glass wire and on the sides of the tubes, both above and below the liquid surface. Figure 16 is a diagram of the tube.

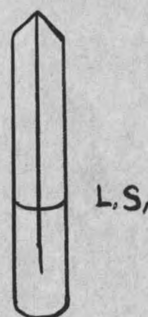


Figure 16

At the end of a month the crystals had the appearance of needles and were approximately 1-2 mm in length. The tubes were taken to Dr. Forbes Robertson, crystalographer, at Montana School of Mines in Butte, Montana, who identified the crystals. The following is a summary of his report:

Optical properties of $Ti(OC_2H_5)_4$

The substance is probably monoclinic.

There are two sets of cleavages which develop. They are not at right angles to each other. Two measurements indicate inclination of about

19°. Extinction parallel to one set, and not to the other. The compound is optically biaxial, negative 2V 80° to 85°.

Indices of refraction.

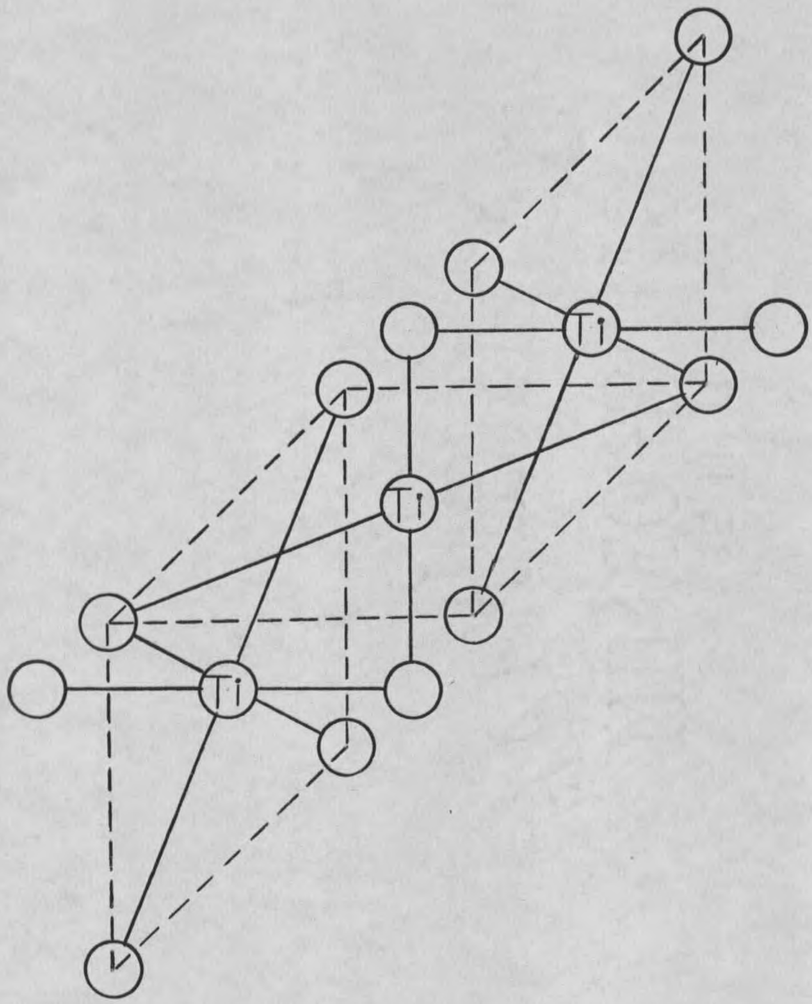
n beta (y) 1.601 more or less.
Determination of other indices only approximate.
n alpha (x) 1.591 or less.
n gamma (z) 1.608 or more.

Birefringence estimate on grain, 0.020 or more, thus the above indices are not necessarily maximum and minimum values. Dispersion, tentative r greater than v. Twinning noted on a few grains, one direction only, optical relations not determined. The material was clear transparent when first removed from the container. It was powdered and kept under cover when not needed. In about an hour's time half of the fragments had hydrolyzed to the extent that valid optical data could not be obtained. However, some grains showed very little alteration after an hour, this included many of the very minute particles.

IX. DISCUSSION OF EXPERIMENTAL RESULTS

The decrease in the curve obtained by plotting the values of the polarization at infinite dilution of $Ti(OC_2H_5)_4$ against the reciprocal of the absolute temperature can not be satisfactorily explained by Debye's equation (3). Since the polarization of polar substances should increase with decreasing temperature according to the Debye equation (3) there is evidence of a negative trend in some factor or factors. When the polarization of polar compounds decreases with decreasing temperature, the contribution arising from the permanent moment may cancel out and the value for the total polarization drop to that of the electronic and atomic polarizations. The sum of the electronic and atomic polarizations, arrived at by refractive index measurements, is approximately 64 Debye units (1). Since the curve decreases slightly in this region and does not fall off to this value, this still indicates a contribution from the permanent moment. However, by an examination of the Debye equation it is seen that the moment would have to be a negative one. If the polarization decreases and increases when plotted against the reciprocal of the absolute temperature, then a possible explanation may be sought in restricted rotation of the groups if the molecules have a tetrahedral configuration which is generally accepted for quadrivalent titanium. Since the curve is approximately linear within this region this does not appear to be the reason.

The association of the ortho-titanates may be due to the fact that titanium has a coordination number of six. In the ortho-titanates there are four oxygen atoms surrounding each titanium atom, therefore, in order for association to occur there may possibly be a distortion of these bonds to permit coordination with pairs of available electrons on oxygens from other molecules. In rutile, a form of TiO_2, each titanium atom is surrounded by six oxygen atoms with bond angles of 90°. Therefore, there may be a possibility that the tetrahedral bonds in the orthotitanates change from 109° to 90° to allow the additional coordination. If the bonds do distort in this manner, then a stable theoretical structure can be proposed in which two molecules of $Ti(OC_2H_5)_4$ are bound to another through three coordinate valences. Additional coordination of the trimer to other monomers could occur but would be less stable due to the fact that only two coordinate bonds would be possible. Therefore, the trimer appears to be the most stable in the proposed structure. Figure 17 is a diagram of the proposed structure of the trimer with the R groups not included.



Proposed Structure for $\left[Ti(OR_4)\right]_3$ with R's not Included

Figure 16

X. SUMMARY

1. The polarization at infinite dilution of $Ti(OC_2H_5)_4$ plotted against the reciprocal of the absolute temperature was found to be approximately a straight line in the region from 17°C to -60°C, decreasing only slightly with decrease in temperature.

2. The association factor of titaniumtetrabutylate, titaniumtetrapropylate, and monochlorotriethoxytitanium has been found to be approximately three.

3. The crystalline structure of titanium-tetraethylate is probably monoclinic.

XI. ACKNOWLEDGEMENTS

The author wishes to take this opportunity to express his sincere appreciation and thanks to Dr. Charles N. Caughlan for his personal guidance and inspiration during this research, and to Dr. Forbes Robertson of Montana School of Mines, for the crystalline identification, and to Dr. C. L. Graverson, also of Montana School of Mines, for his help and advice. He also wishes to thank the Research Corporation of New York for making this investigation possible.

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