



Structural studies of titanium alkoxides
by Robert Dale Witters

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:

Dipole moments of four alkyl titanates were determined in n-heptane solution by the method Halverstadt and Kumler. It was found that the values obtained for the ethyl, n-propyl, and n-butyl orthoesters were for the trimers, but those found for tert-butyl titanate were for the monomers. Variations of the dipole moments of these compounds with temperature change indicate the potential energy barrier to rotation of the alkoxy groups is of magnitude kT .

The crystal and molecular structures of monomethyltriethyl titanate was determined by x-ray diffraction techniques. Crystal data obtained are: $a = 12.14 \text{ \AA}$ $\alpha = 76^\circ 56'$ density (meas.) = 1.244 g/cc $b = 12.13$ $\beta = 77^\circ 2'$ density (calc.) = 1.236 g/cc $c = 16.93$ $\gamma = 74^\circ 15'$ $Z = 8$ Space Group P1 In the solid state the molecules are linked together to form tetramer units. In the tetramers the four titanium atoms form a planar diamond shape, sharing oxygen atoms so that each titanium atom has a coordination number of six.

A preliminary investigation of an hydrolysis product of tetraethyl titanate was carried out. The unit cell of this crystal contains approximately 60 titanium atoms. Due to the complexity of this crystal and also to the fact that the molecular formula of the compound is uncertain, the structure determination was not completed. Crystal data obtained for this compound are: $a = 27.92 \text{ \AA}$ density = 1.305 g/cc $b = 22.40$ space group P21/a $c = 23.30$ $\beta = 117^\circ 15'$

STRUCTURAL STUDIES OF TITANIUM ALKOXIDES

by

ROBERT DALE WITTERS

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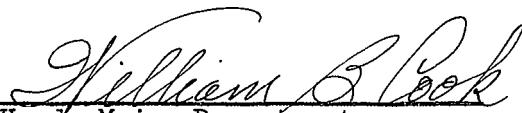
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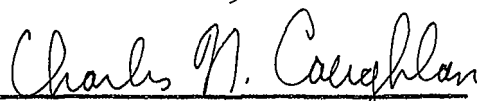
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ABSTRACT

Dipole moments of four alkyl titanates were determined in n-heptane solution by the method Halverstadt and Kumler. It was found that the values obtained for the ethyl, n-propyl, and n-butyl orthoesters were for the trimers, but those found for tert-butyl titanate were for the monomers. Variations of the dipole moments of these compounds with temperature change indicate the potential energy barrier to rotation of the alkoxy groups is of magnitude kT .

The crystal and molecular structures of monomethyltriethyl titanate was determined by x-ray diffraction techniques. Crystal data obtained are:

$$\begin{array}{lll}
 a = 12.14 \text{ \AA} & \alpha = 76^{\circ}56' & \text{density (meas.)} = 1.244 \text{ g/cc} \\
 b = 12.13 & \beta = 77^{\circ}2' & \text{density (calc.)} = 1.236 \text{ g/cc} \\
 c = 16.93 & \gamma = 74^{\circ}15' & Z = 8
 \end{array}$$

Space Group $P1$

In the solid state the molecules are linked together to form tetramer units. In the tetramers the four titanium atoms form a planar diamond shape, sharing oxygen atoms so that each titanium atom has a coordination number of six.

A preliminary investigation of an hydrolysis product of tetraethyl titanate was carried out. The unit cell of this crystal contains approximately 60 titanium atoms. Due to the complexity of this crystal and also to the fact that the molecular formula of the compound is uncertain, the structure determination was not completed. Crystal data obtained for this compound are:

$$\begin{array}{ll}
 a = 27.92 \text{ \AA} & \text{density} = 1.305 \text{ g/cc} \\
 b = 22.40 & \text{space group } P2_1/a \\
 c = 23.30 \\
 \beta = 117^{\circ}15'
 \end{array}$$

INTRODUCTION

The chemistry of organic compounds of titanium has been of interest for a number of years. In many ways the organic titanates exhibit unusual properties, some of which have lead to industrial uses in the paint and the electrical industries. To a large extent, however, understanding of their chemistry has been limited because the structures were not known. Only in very recent years have attempts been made to determine their structures by any of the various methods now used. The research reported in this dissertation is an attempt to provide some of the first accurate structural information about these compounds. Before describing the methods and results a brief review of the knowledge available at present will be given.

Gilman and Jones⁽²⁴⁾ have summarized early attempts to prepare organic titanium compounds. In 1875 Demarcay⁽²¹⁾ reported the first preparation of an alkyl titanate, but later investigators⁽³¹⁾ were unable to duplicate his work and showed that his compounds were probably a mixture of oxy-ethyl titanates. Probably the first preparation of a pure alkyl titanate was carried out in 1923 by Bischoff and Adkins⁽¹⁾. They reported obtaining the tetraethyl, tetraisopropyl, and tetramethyl titanates.

Since the early 1940's chemists have become concerned with the structures of these compounds and the mechanisms of their reactions, particularly with water. All of the alkyl titanates react with water, the rate of reaction generally increasing with decreasing molecular weight of the compound.

Much of the work carried on in this laboratory and described in this dissertation began with the investigation of tetraethyl titanate, as this

is probably the most unusual of this group. For several years it was reported in the literature to be a liquid at room temperature; however in 1950 Caughlan and Crowe⁽¹⁵⁾ showed that its normal state is solid. The pure compound is obtained as a liquid by distillation. If the liquid is allowed to stand for a considerable length of time, usually several months, small crystals form on the sides of the container, and eventually the entire liquid solidifies.

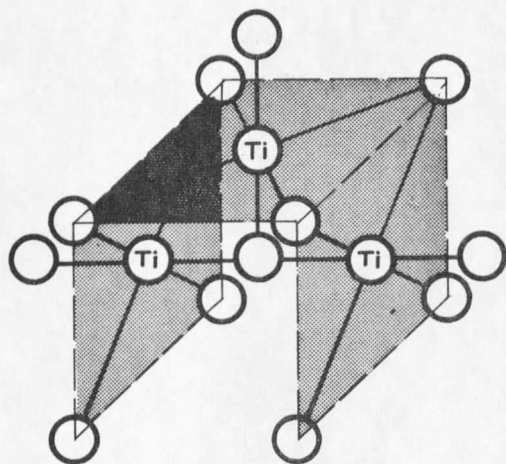
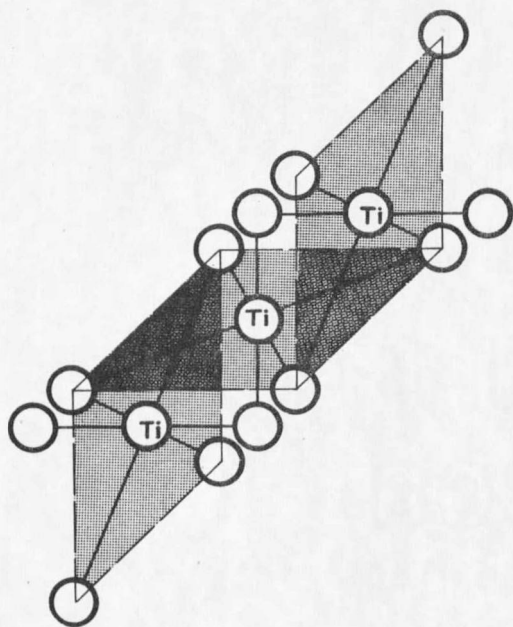
In this laboratory research on organic titanates started with a study of the dielectric properties of these compounds and the molecular weights in solution. Results of the molecular weight investigations showed that all of the orthoesters studied had an association number of three⁽¹³⁾. This association is not surprising when one considers the fact that the coordination number of titanium is six, whereas its primary valence number in the monomeric titanate is only four. To satisfy the coordination number of six, oxygens from surrounding titanate molecules must be used. The structures proposed for the trimer are shown in Figure 1; the linear structure in Figure 1a is the one that most generally has been accepted.

As already mentioned most of the alkyl titanates react readily with water. For small amounts of water the major products of the reaction are polymers, the size of the polymer depending on the amount of water added. D. C. Bradley and his associates have made a very thorough investigation of the hydrolysis of $Ti(OC_2H_5)_4$ and, based on the trimer structure proposed by Caughlan, have proposed a set of reactions for the hydrolysis and structures for the hydrolysis products (2), (3), (4).

In order to confirm the trimeric structure of the alkyl titanates it was decided to determine the structure of the tetraethyl titanate by single crystal x-ray diffraction techniques. Crystals were obtained from an ethanol solution, and cell dimensions were determined from x-ray data. It was apparent in the early stages of this investigation that the crystals were not of the tetraethylate but of one of the hydrolysis products. Since good crystals of the hydrolysis product were now on hand, it was decided to continue the x-ray structure determination of this compound.

Crystals of monomethyltriethyl titanate were obtained by the method described by Varma and Mehrotra⁽³⁴⁾. Since this compound is also trimeric in solution, determination of this structure would serve to verify that proposed for the trimers. Accordingly, a major portion of this research is on the structure of $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$.

In addition to the x-ray examination of the two crystals mentioned, the dielectric properties of tetraethyl titanate, tetra-n-propyl titanate, tetra-tert-butyl titanate, and tetra-n-butyl titanate have been measured in n-heptane at 0°, 25°, and 50°C.



Proposed Structures for Trimeric Titanium Tetraethylate

(Carbons not Shown)

Figure 1

PART I

Dielectric Studies of Alkyl Titanates

The dipole moment of a compound is determined by its molecular structure. Aside from translational or rotational motion of the molecule as a whole, its atoms are not in fixed locations; they are in constant vibration about an average point, and atoms or groups of atoms may rotate about some bond in the molecule. Greater vibrations of the atoms at increased temperatures generally have little effect on the dipole moment since the average positions of the atoms are not changed. The degree to which an atom or group of atoms rotate about an axis may be affected by temperature, however, thus changing the dipole moment of the molecule. Comparison of measured and theoretically calculated dipole moments for alkyl titanates has indicated restriction of rotation of the alkoxy groups.

This dielectric study of the titanates was therefore undertaken to learn how the dipole moments are affected by temperature. From this, insight into the degree of restriction of rotation of the groups and to the energy barrier to rotation may be obtained.

Theory and Discussion of Methods

A detailed review of the theory of dielectric constants, polarization, and dipole moment may be found in the references (14), (20), and (29). However a brief discussion of the general theory will be given here.

Molecules, although neutral, possess small centers of negative and positive charges. In polar molecules there is a finite distance of separation between the centers of the negative and positive charges, and the

polarity of a molecule becomes less as these centers approach each other. When placed in an electric field a polar molecule will tend to orient itself, the charges lining up in the direction of the field. The force required to orient the molecule depends on the magnitude of the charges and on the distance between them. The dipole moment is a measure of these two quantities; it is the product of either charge e by the distance between them: $\mu = er$. It serves as a useful quantitative measure of the extent to which a molecule is polar. Thus dipole, or dielectric, studies provide some information concerning the shape of a molecule.

The dielectric constant of a substance is related to its degree of polarization in an electric field. Polarization is determined in this research by determining the extent to which the substance in the dissolved state in a solution of a nonpolar solvent contributes to the dielectric constant of the solution. By extrapolating the measurements of dielectric constant to infinite dilution, a value is obtained which corresponds to a situation in which the molecules are so far apart that they do not induce charges in each other.

The molar polarization of a substance can be calculated from the dielectric constant ϵ using a formula developed by Clausius and Mosotti on the basis of theories of electric charges induced by electric field:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d}$$

where P is the molar polarization, M the molecular weight, and d the density.

For a binary solution the equation can be written as

$$P_{12} = c_1 P_1 + c_2 P_2 = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot \frac{c_1 M_1 + c_2 M_2}{d_{12}}$$

where P is the molar polarization, ϵ the dielectric constant, d the density, c the concentration, and M molecular weight. The subscripts 1, 2, and 12 refer to solvent, solute, and solution, resp.

Assuming the dielectric constant and the specific volume of a binary solution to be linear functions of concentration, Halverstadt and Kumler⁽²⁵⁾ arrived at the following equation:

$$P_{\infty} = \frac{\epsilon_1}{\epsilon_1} \frac{-1}{+2} (M_2 v_1 + M_1 B) + \frac{3Av_1 M_1}{(\epsilon_1 + 2)^2},$$

where the meanings of the symbols are as follows:

P_{∞} is the molar polarization of solute at infinite dilution

ϵ_1 is the dielectric constant of solution at infinite dilution (intercept)

v_1 is the specific volume of solution at infinite dilution (intercept)

M_1 and M_2 are the molecular weights of solvent and solute, resp.

A is the slope of the dielectric constant-concentration curve

B is the slope of the specific volume-concentration curve.

The method of Halverstadt and Kumler takes into account the fact that the dielectric constant of the solvent may be considerably different from the measured dielectric constant of the pure solvent. This may be due partially to the absorption of water. This solvent polarization error is essentially eliminated by obtaining the dielectric constant of the pure solvent from extrapolation to infinite dilution. These authors point out that solvents with a low dielectric constant must be used.

The molar polarization determined by this method is the total polarization and is the sum of the orientation polarization, the atomic polarization, and the electronic polarization. The dipole moment of a

molecule can be calculated from the orientation polarization. Thus the atomic and electronic polarizations must be determined and subtracted from P_{∞} . Hence, $P_{\mu} = P_{\infty} - P_e - P_a$ where P_{μ} , P_{∞} , P_e , and P_a are the orientation, total, electronic, and atomic polarizations, resp.

The electronic polarization and molar refraction of a compound theoretically are the same for a high frequency oscillating electric field. According to Maxwell's relation, $\epsilon = n^2$ for a non-polar substance, where n is the refractive index. Thus n^2 is really a measure of the dielectric constant with the effects of the permanent dipoles and atomic effects removed. The reason for this is that the frequencies of optical light are so great that the dipoles of the molecules are unable to orient themselves fast enough, and only the effects due to electronic polarization are manifest. Thus by determining the refractive index of a substance, and its density, the electronic polarization may be determined. The molar refraction R is given by the relation $R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$.

The atomic polarization is not so easily determined. This contribution to the total polarization is usually quite small and is frequently omitted from calculations; sometimes it is assumed to be about 5% of the electronic polarization. In this work on titanium alkoxides the effect due to the atomic polarization has been neglected. Thus in this case the orientation polarization is calculated by subtracting the molar refraction from P_{∞} : $P_{\mu} = P_{\infty} - R - P_a$ where it is assumed that $P_a \approx 0$.

The dipole moment of a compound can be calculated from the orientation polarization by the equation

$$\mu = 0.0127 \times 10^{-18} \sqrt{P_{\mu} T} \text{ e.s.u.} = \sqrt{P_{\mu} T} \text{ Debye.}$$

A. Preparation of Compounds

The tetraethyl and tetra-n-propyl titanates were prepared by the sodium alkoxide method.⁽¹⁾⁽³¹⁾ Tetra-tert-butyl titanate was prepared by the pyridine-ammonia method,⁽⁵⁾⁽¹⁹⁾ while the n-butyl ester was obtained from E. I. duPont de Nemours and Co., Inc.

B. Dielectric Constant Apparatus

The electric circuit, the precision condenser, and the dielectric cell have been described before.⁽¹⁴⁾⁽¹⁵⁾ The dielectric cell was modified slightly by placing a thermostated reservoir on top of the cell, increasing the effective volume of the unit from 10 ml to about 25 ml. An opening in the top of the reservoir permitted inserting a metal thermister directly into the dielectric cell for accurate temperature measurement. A second opening permitted addition of solute to the solution in the cell. Both openings in the reservoir were sealed with ground glass stoppers so no evaporation of solvent nor absorption of water could take place except during the brief periods when solute was being added.

C. Density Apparatus

Densities of the solutions at 25° and at 50°C were obtained by the Westphal balance method. An analytic balance was modified for this purpose. A plummet of 15.65 ml capacity was made by sealing several grams of mercury into a glass tube. The solutions were placed in a thermostated container (80 ml) for the readings. Additional solute was easily added to this, the mixture being stirred by moving the bob up and down. A cork stopper sealed the solution from contact with air except for a small hole for the wire leading from the balance to the plummet.

A National Bureau of Standards thermometer also was immersed in the solution.

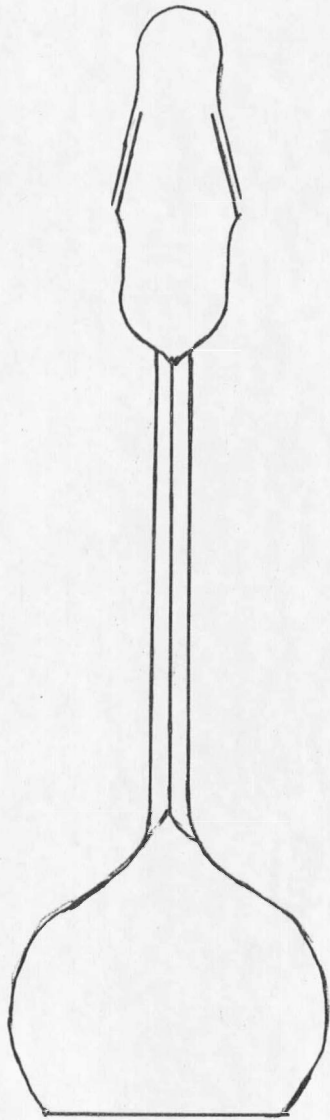
This method of determining densities of the solutions was very satisfactory for measurements at 25° and 50°C. However at zero degrees this apparatus gave very poor results due to rapid absorption of moisture from the air, hydrolyzing the solute. Placing the apparatus in a dry box did not help matters.

For low temperature density measurements two pycnometers (Figure 2) were made, one with a volume of 33.02 ml, the other with a volume of 30.73 ml at 0°C. The bulb of the pycnometer was attached by a capillary to a reservoir which was sealed off from the air by a ground glass stopper. The unit was immersed in a bath at the desired temperature. After thermal equilibrium was established, the volume of the solution was adjusted by removing excess liquid by a very fine capillary connected to an aspirator.

D. Temperature Control and Measurement

For density measurements temperature was maintained for the 25° and 50° runs by circulating water through the jacket of the cell, the water coming from a thermostat. Temperature of the solution in the cell was measured by a calibrated N.B.S. thermometer. Temperature at 0°C was obtained by immersing the pycnometers directly into a water-ice mixture in a Dewar flask.

Temperature of the solutions in the dielectric cell was obtained by passing a liquid (water at 25° and 50°, isopropyl alcohol at 0°) through the jacket of the cell. A constant temperature bath was used at



Pycnometer

Figure 2

the two higher temperatures, a refrigeration unit at the lower temperature. Temperature in the cell itself was determined by measuring the resistance of a metal thermister inserted in the inner cavity of the cylindrical capacitance unit. The thermister was calibrated against the N.B.S. thermometer.

E. Data and Results

The calibration of the pycnometer at 0° and of the dielectric cell at 0°, 25°, and 50° was made using n-heptane as a standard. The dielectric constants of heptane which were used at these temperatures are those reported by Dornte and Smyth;⁽²²⁾ densities are those given by Smyth and Stoops.⁽³⁰⁾ The capacitance of the dielectric cell was determined at the start of each run.

The n-heptane used in these determinations was obtained from Phillips Petroleum Co. and was dried by distillation from sodium.

Dielectric constants and densities were determined as described. Results of these measurements are tabulated in Tables I through X and depicted in Figures 3 through 22. Molar polarizations at infinite dilution were calculated by the method of Halverstadt and Kumler as described on page 6. The slopes and intercepts of the dielectric constant-mole fraction and specific volume-mole fraction curves were obtained by the method of least squares.

For the calculations involved, a program was written for the I.B.M. 650 computer. This program computed the intercepts and slopes of the dielectric constant and specific volume versus mole fraction curves by the method of least squares, and also calculated the total

polarization and the dipole moment. Results of these calculations are shown in Table XI. Values for the refractive indices and densities of the pure liquids are given in Table XII.

In the compounds investigated there is the possibility of rotation of the hydrocarbon chains about the titanium-oxygen bonds. If there is restriction of rotation, the dipole moment should be a function of temperature. As the temperature is increased, more thermal energy is available to overcome the potential energy barrier to rotation. Thus the dipole moment should vary with temperature and approach the theoretical value calculated assuming complete freedom of rotation. Using the Eyring equation⁽²³⁾ Crowe and Caughlan⁽¹⁵⁾ calculated the dipole moment of titanium tetraethoxide assuming complete freedom of rotation of the ethoxy groups and obtained a value of 2.11D.

Figure 23 shows graphically the variation of dipole moment of the ethyl, n-propyl, and n-butyl esters with temperature. The dipole moment of each is seen to increase with temperature toward the computed value of 2.11D for the ethyl titanate, indicating that the molecules do not exhibit complete freedom of rotation. This result suggests that the potential energy barrier is of the same order of magnitude as the thermal energy, i.e., kT .

Tetraethyl Titanate

Table I

| <u>Temperature</u> | <u>Dielectric Constant Values</u> | | <u>Specific Volume Values</u> | |
|--------------------|-----------------------------------|----------------------------|-------------------------------|------------------------|
| | <u>mole fraction</u> | <u>dielectric constant</u> | <u>mole fraction</u> | <u>specific volume</u> |
| 50° | 0.006412 | 1.8944 | 0.001114 | 1.5189 |
| | .008535 | 1.8985 | .002442 | 1.5171 |
| | .007135 | 1.8957 | .003686 | 1.5155 |
| | .003340 | 1.8888 | .004894 | 1.5138 |
| | .004849 | 1.8916 | .006085 | 1.5124 |
| | .004826 | 1.8916 | .007409 | 1.5106 |
| | .009506 | 1.9005 | .000000 | 1.5205 |
| | .003598 | 1.8900 | | |
| | .004679 | 1.8908 | | |
| | .001959 | 1.8851 | | |
| | .000000 | 1.8810 | | |

Tetraethyl Titanate

Table II

| <u>Temperature</u> | <u>Dielectric Constant Values</u> | | <u>Specific Volume Values</u> | |
|--------------------|-----------------------------------|----------------------------|-------------------------------|------------------------|
| | <u>mole fraction</u> | <u>dielectric constant</u> | <u>mole fraction</u> | <u>specific volume</u> |
| 25° | 0.004844 | 1.9289 | 0.000942 | 1.4702 |
| | .005553 | 1.9305 | .002110 | 1.4687 |
| | .003875 | 1.9265 | .003031 | 1.4676 |
| | .007396 | 1.9338 | .004004 | 1.4663 |
| | .003633 | 1.9273 | .004975 | 1.4652 |
| | .003911 | 1.9273 | .006596 | 1.4632 |
| | .005824 | 1.9310 | .000000 | 1.4713 |
| | .007705 | 1.9346 | | |
| | .004567 | 1.9277 | | |
| | .002015 | 1.9220 | | |
| | .009035 | 1.9363 | | |
| | .000000 | 1.9180 | | |

Tetraethyl Titanate

Table III

| <u>Temperature</u> | <u>Dielectric Constant Values</u> | | <u>Specific Volume Values</u> | |
|--------------------|-----------------------------------|----------------------------|-------------------------------|------------------------|
| | <u>mole fraction</u> | <u>dielectric constant</u> | <u>mole fraction</u> | <u>specific volume</u> |
| 0°C | 0.006281 | 1.9671 | 0.026517 | 1.3961 |
| | .004279 | 1.9622 | .018505 | 1.4055 |
| | .002840 | 1.9597 | .012689 | 1.4125 |
| | .008256 | 1.9715 | .009174 | 1.4168 |
| | .004876 | 1.9638 | .000000 | 1.4278 |
| | .004626 | 1.9638 | | |
| | .002860 | 1.9597 | | |
| | .006476 | 1.9675 | | |
| | .006499 | 1.9678 | | |
| | .005259 | 1.9650 | | |
| | .000000 | 1.9540 | | |

Tetrapropyl Titanate

Table IV

| <u>Temperature</u> | <u>Dielectric Constant Values</u> | | <u>Specific Volume Values</u> | |
|--------------------|-----------------------------------|----------------------------|-------------------------------|------------------------|
| | <u>mole fraction</u> | <u>dielectric constant</u> | <u>mole fraction</u> | <u>specific volume</u> |
| 50° | 0.004170 | 1.8892 | 0.002214 | 1.5169 |
| | .005630 | 1.8932 | .003541 | 1.5149 |
| | .003092 | 1.8883 | .005200 | 1.5122 |
| | .010429 | 1.9037 | .006959 | 1.5098 |
| | .007441 | 1.8977 | .008907 | 1.5070 |
| | .007228 | 1.8969 | .000000 | 1.5205 |
| | .004293 | 1.8908 | | |
| | .006476 | 1.8957 | | |
| | .010867 | 1.9042 | | |
| | .003823 | 1.8892 | | |
| | .000000 | 1.8810 | | |

Tetrapropyl Titanate

Table V

| <u>Temperature</u> | <u>Dielectric Constant Values</u> | | <u>Specific Volume Values</u> | |
|--------------------|-----------------------------------|----------------------------|-------------------------------|------------------------|
| | <u>mole fraction</u> | <u>dielectric constant</u> | <u>mole fraction</u> | <u>specific volume</u> |
| 25°C | 0.005723 | 1.9313 | 0.000456 | 1.4705 |
| | .003013 | 1.9261 | .001276 | 1.4694 |
| | .005762 | 1.9310 | .002206 | 1.4680 |
| | .003622 | 1.9265 | .003385 | 1.4661 |
| | .006229 | 1.9322 | .004358 | 1.4649 |
| | .003499 | 1.9265 | .005409 | 1.4634 |
| | .003755 | 1.9269 | .000000 | 1.4713 |
| | .002375 | 1.9240 | | |
| | .009647 | 1.9391 | | |
| | .005315 | 1.9301 | | |
| | .007352 | 1.9344 | | |
| | .000000 | 1.9180 | | |

Tetrapropyl Titanate

Table VI

| <u>Temperature</u> | <u>Dielectric Constant Values</u> | | <u>Specific Volume Values</u> | |
|--------------------|-----------------------------------|----------------------------|-------------------------------|------------------------|
| | <u>mole fraction</u> | <u>dielectric constant</u> | <u>mole fraction</u> | <u>specific volume</u> |
| 0°C | 0.006119 | 1.9679 | 0.013070 | 1.4102 |
| | .005425 | 1.9679 | .008754 | 1.4161 |
| | .001837 | 1.9589 | .006053 | 1.4197 |
| | .008402 | 1.9736 | .003995 | 1.4225 |
| | .002579 | 1.9609 | .002863 | 1.4240 |
| | .005575 | 1.9670 | .000000 | 1.4278 |
| | .003418 | 1.9626 | | |
| | .006580 | 1.9695 | | |
| | .002777 | 1.9611 | | |
| | .005930 | 1.9675 | | |
| | .010924 | 1.9784 | | |
| | .000000 | 1.9540 | | |

Tetra-n-butyl Titanate

Table VII

| <u>Temperature</u> | <u>Dielectric Constant Values</u> | | <u>Specific Volume Values</u> | |
|--------------------|-----------------------------------|----------------------------|-------------------------------|------------------------|
| | <u>mole fraction</u> | <u>dielectric constant</u> | <u>mole fraction</u> | <u>specific volume</u> |
| 50°C | 0.002636 | 1.8879 | 0.001418 | 1.5182 |
| | .003384 | 1.8891 | .002721 | 1.5160 |
| | .009277 | 1.9013 | .004060 | 1.5137 |
| | .002555 | 1.8875 | .005265 | 1.5116 |
| | .005285 | 1.8924 | .006587 | 1.5092 |
| | .004861 | 1.8920 | .007932 | 1.5070 |
| | .009510 | 1.9034 | .000000 | 1.5205 |
| | .004728 | 1.8916 | | |
| | .005445 | 1.8932 | | |
| | .003993 | 1.8900 | | |
| | .005833 | 1.8944 | | |
| | .008346 | 1.9005 | | |
| | .000917 | 1.8846 | | |
| | .007346 | 1.8976 | | |
| | .002251 | 1.8871 | | |
| | .001108 | 1.8847 | | |
| .000000 | 1.8810 | | | |

Tetra-n-butyl Titanate

Table VIII

| <u>Temperature</u> | <u>Dielectric Constant Values</u> | | <u>Specific Volume Values</u> | |
|--------------------|-----------------------------------|----------------------------|-------------------------------|------------------------|
| | <u>mole fraction</u> | <u>dielectric constant</u> | <u>mole fraction</u> | <u>specific volume</u> |
| 25°C | 0.003964 | 1.9285 | 0.000944 | 1.4697 |
| | .002845 | 1.9249 | .001911 | 1.4681 |
| | .006618 | 1.9338 | .002642 | 1.4672 |
| | .001949 | 1.9236 | .003414 | 1.4660 |
| | .005114 | 1.9301 | .004168 | 1.4646 |
| | .001959 | 1.9232 | .005067 | 1.4634 |
| | .003675 | 1.9273 | .000000 | 1.4713 |
| | .004093 | 1.9281 | | |
| | .005286 | 1.9301 | | |
| | .000000 | 1.9180 | | |
| | .006321 | 1.9326 | | |

Tetra-n-butyl Titanate

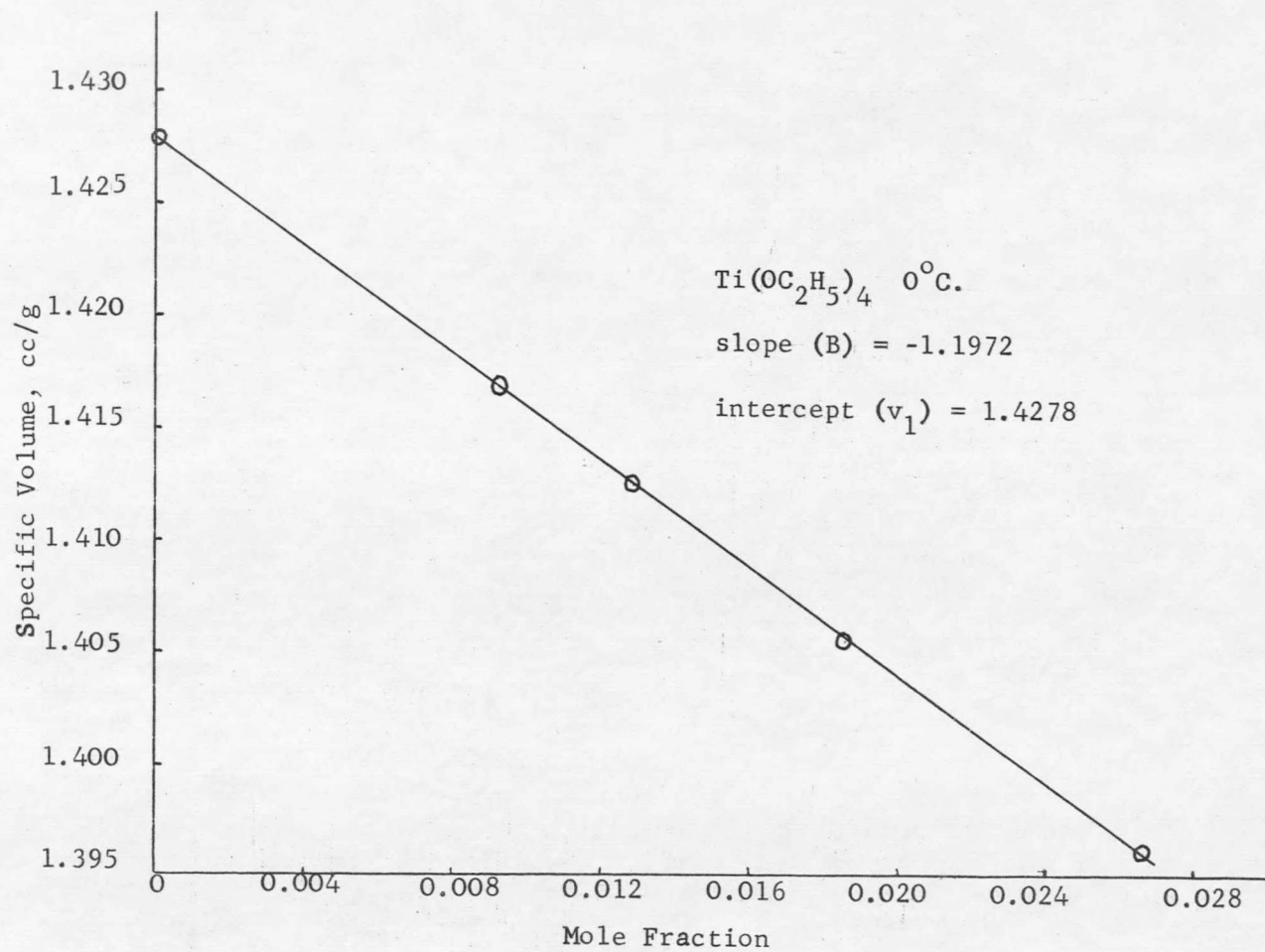
Table IX

| <u>Temperature</u> | <u>Dielectric Constant Values</u> | | <u>Specific Volume Values</u> | |
|--------------------|-----------------------------------|----------------------------|-------------------------------|------------------------|
| | <u>mole fraction</u> | <u>dielectric constant</u> | <u>mole fraction</u> | <u>specific volume</u> |
| 0°C | 0.004616 | 1.9658 | 0.001711 | 1.4252 |
| | .005135 | 1.9666 | .001278 | 1.4259 |
| | .003003 | 1.9610 | .003013 | 1.4233 |
| | .006410 | 1.9695 | .003415 | 1.4226 |
| | .002782 | 1.9617 | .003742 | 1.4223 |
| | .002626 | 1.9609 | .001268 | 1.4259 |
| | .007667 | 1.9727 | .000000 | 1.4278 |
| | .006703 | 1.9695 | | |
| | .002549 | 1.9613 | | |
| | .008611 | 1.9748 | | |
| | .002860 | 1.9617 | | |
| | .000000 | 1.9540 | | |

Tetra-tert-butyl Titanate

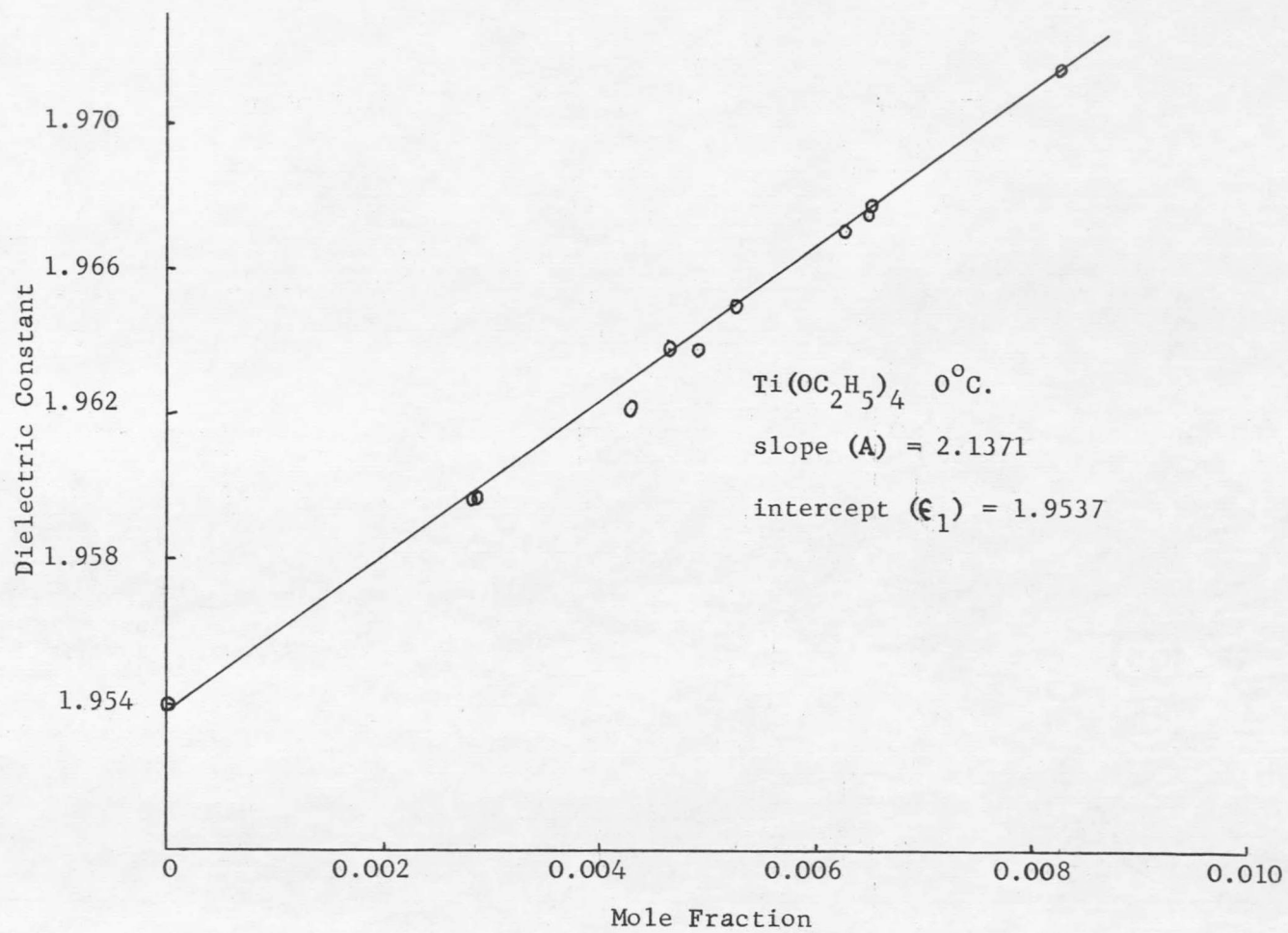
Table X

| <u>Temperature</u> | <u>Dielectric Constant Values</u> | | <u>Specific Volume Values</u> | |
|--------------------|-----------------------------------|----------------------------|-------------------------------|------------------------|
| | <u>mole fraction</u> | <u>dielectric constant</u> | <u>mole fraction</u> | <u>specific volume</u> |
| 25°C | 0.000000 | 1.9180 | 0.000779 | 1.4705 |
| | .001290 | 1.9215 | .001536 | 1.4696 |
| | .002295 | 1.9239 | .002326 | 1.4688 |
| | .003385 | 1.9272 | .003150 | 1.4678 |
| | .004486 | 1.9304 | .004101 | 1.4667 |
| | .005017 | 1.9318 | .005216 | 1.4654 |
| | .005970 | 1.9345 | .000000 | 1.4713 |
| | .006727 | 1.9365 | | |
| | .007204 | 1.9383 | | |
| | .008103 | 1.9410 | | |



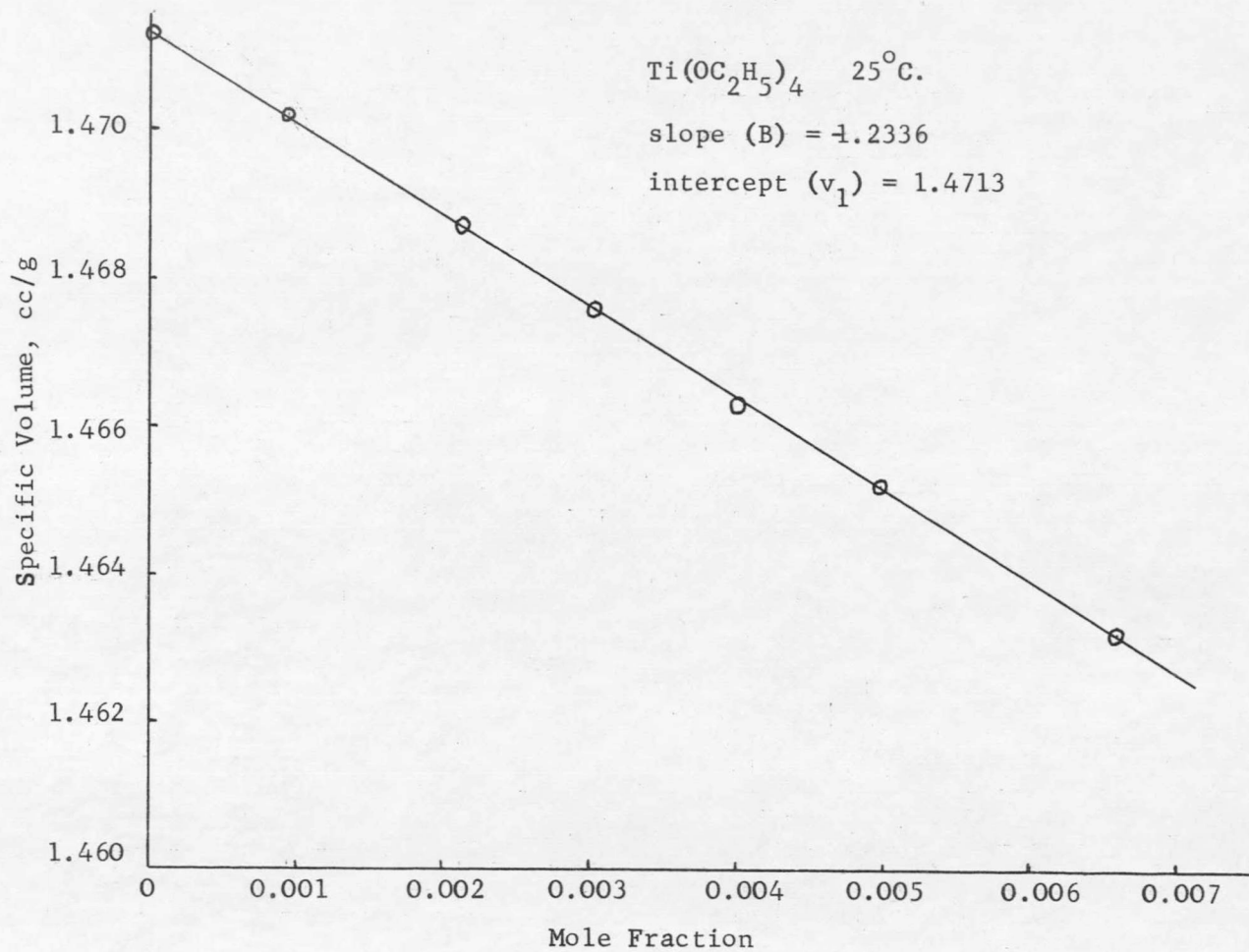
Specific Volume vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_2\text{H}_5)_4$, 0°C .

Figure 3



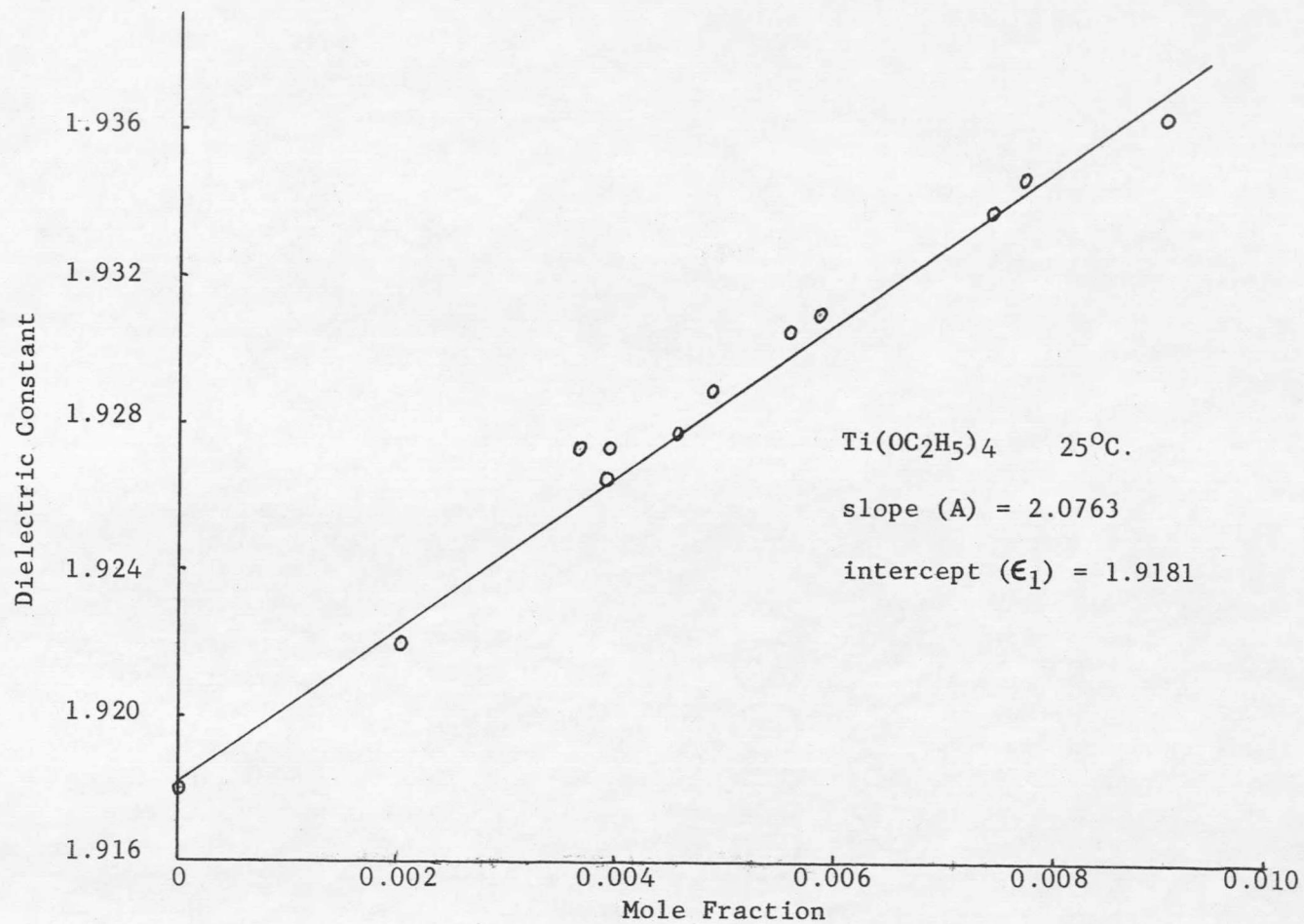
Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_2\text{H}_5)_4$, 0°C .

Figure 4



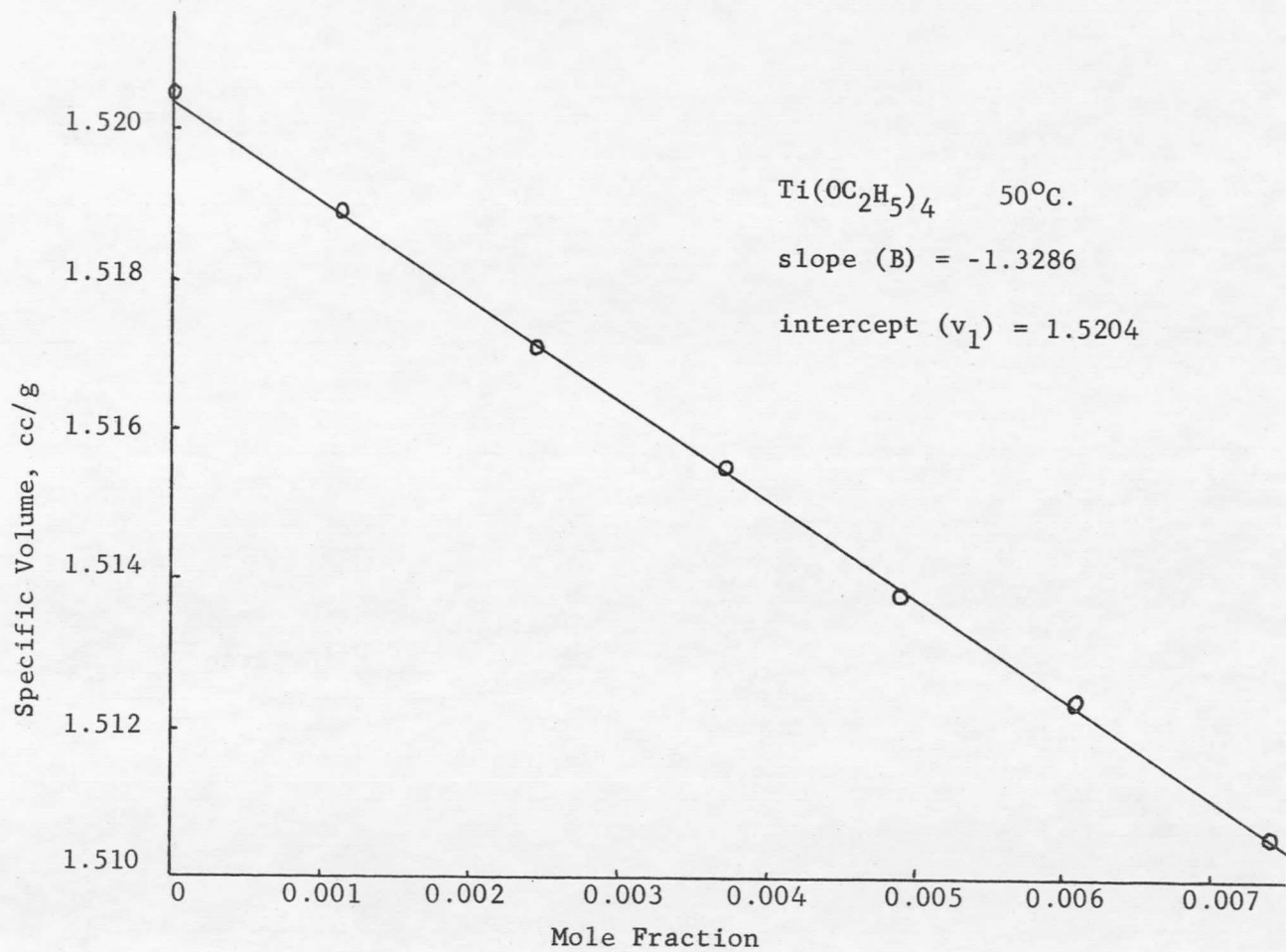
Specific Volume vs. Mole Fraction Curve for Ti(OC₂H₅)₄, 25°C.

Figure 5



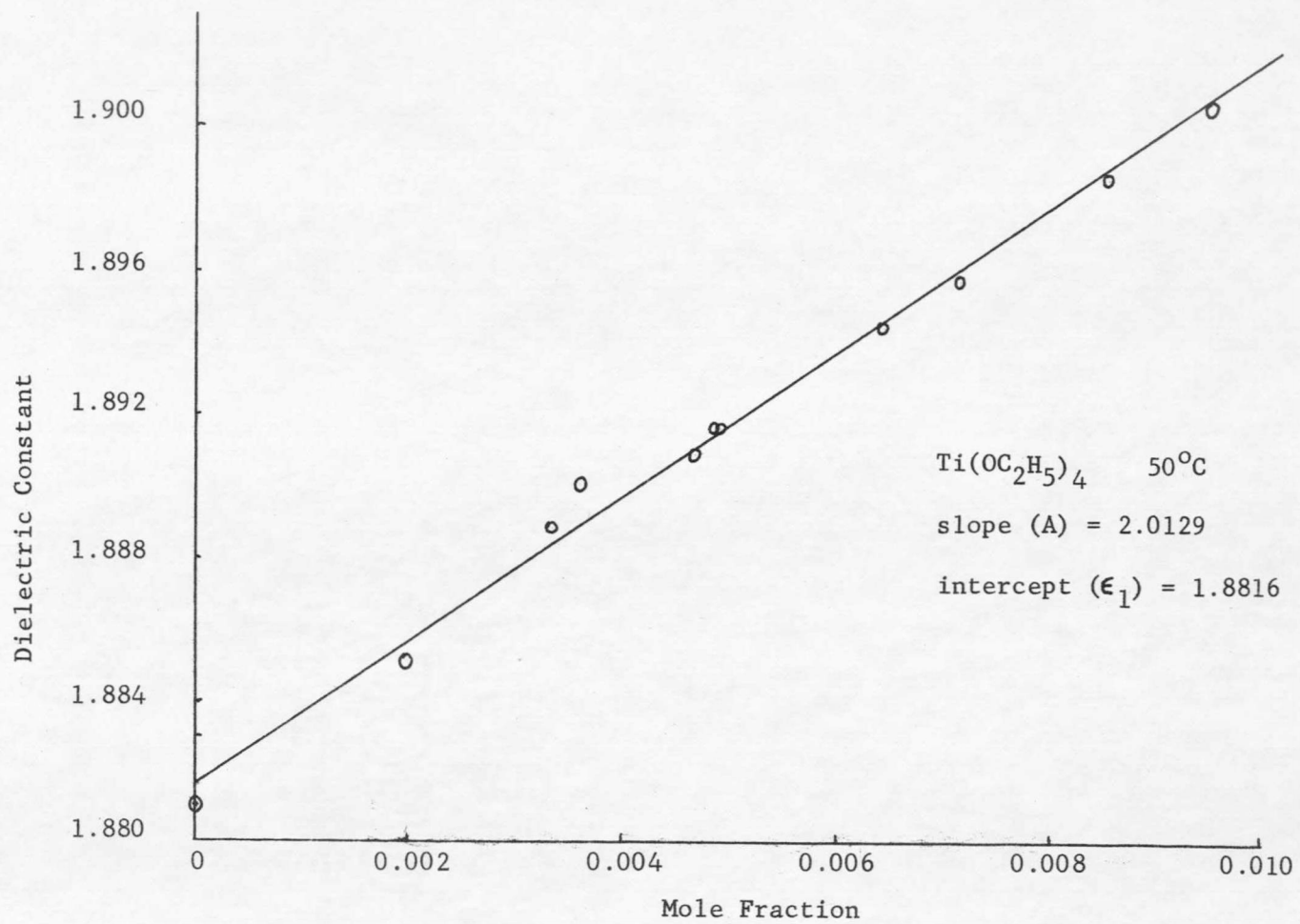
Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_2\text{H}_5)_4$, 25°C

Figure 6



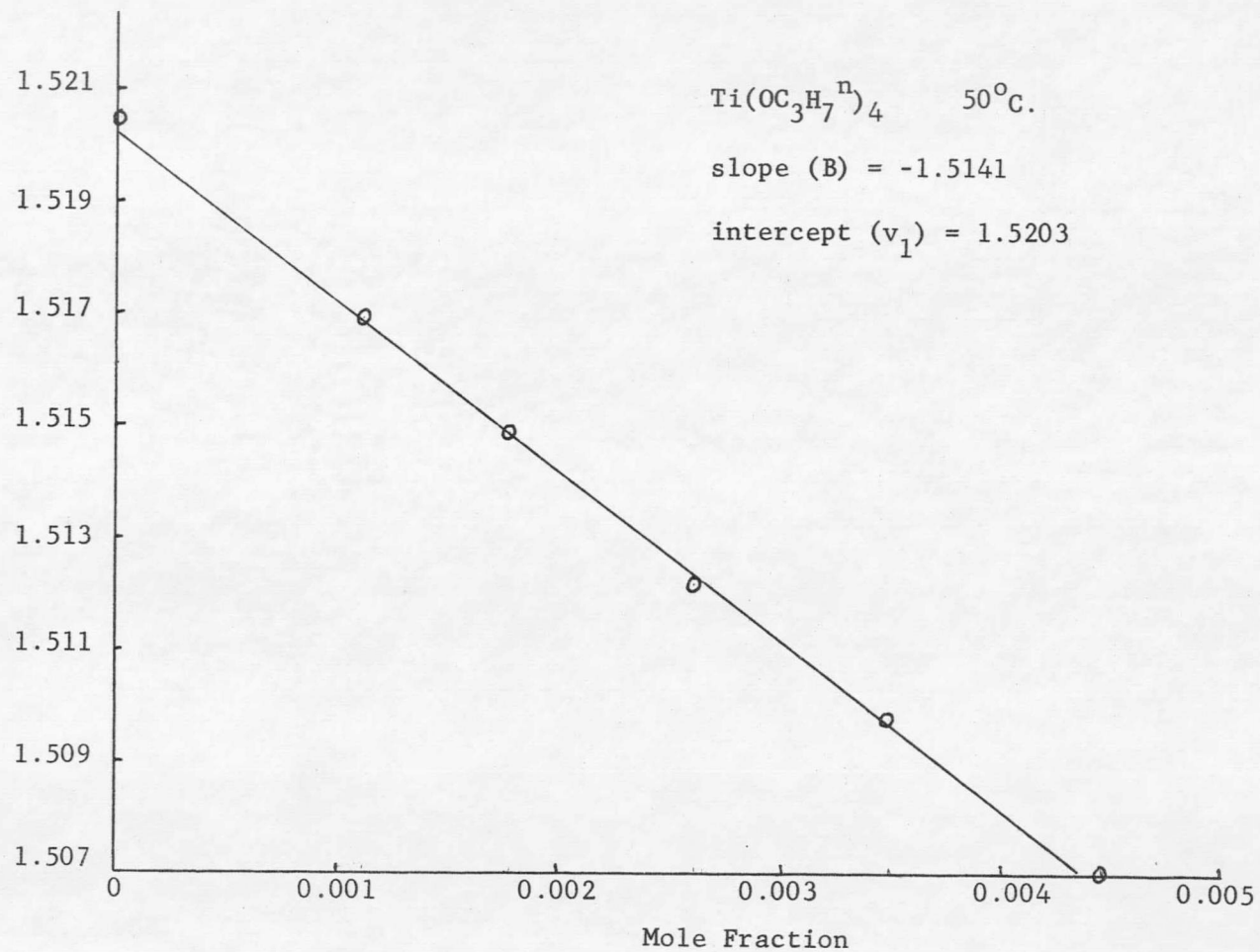
Specific Volume vs. Mole Fraction Curve for Ti(OC₂H₅)₄, 50°C.

Figure 7



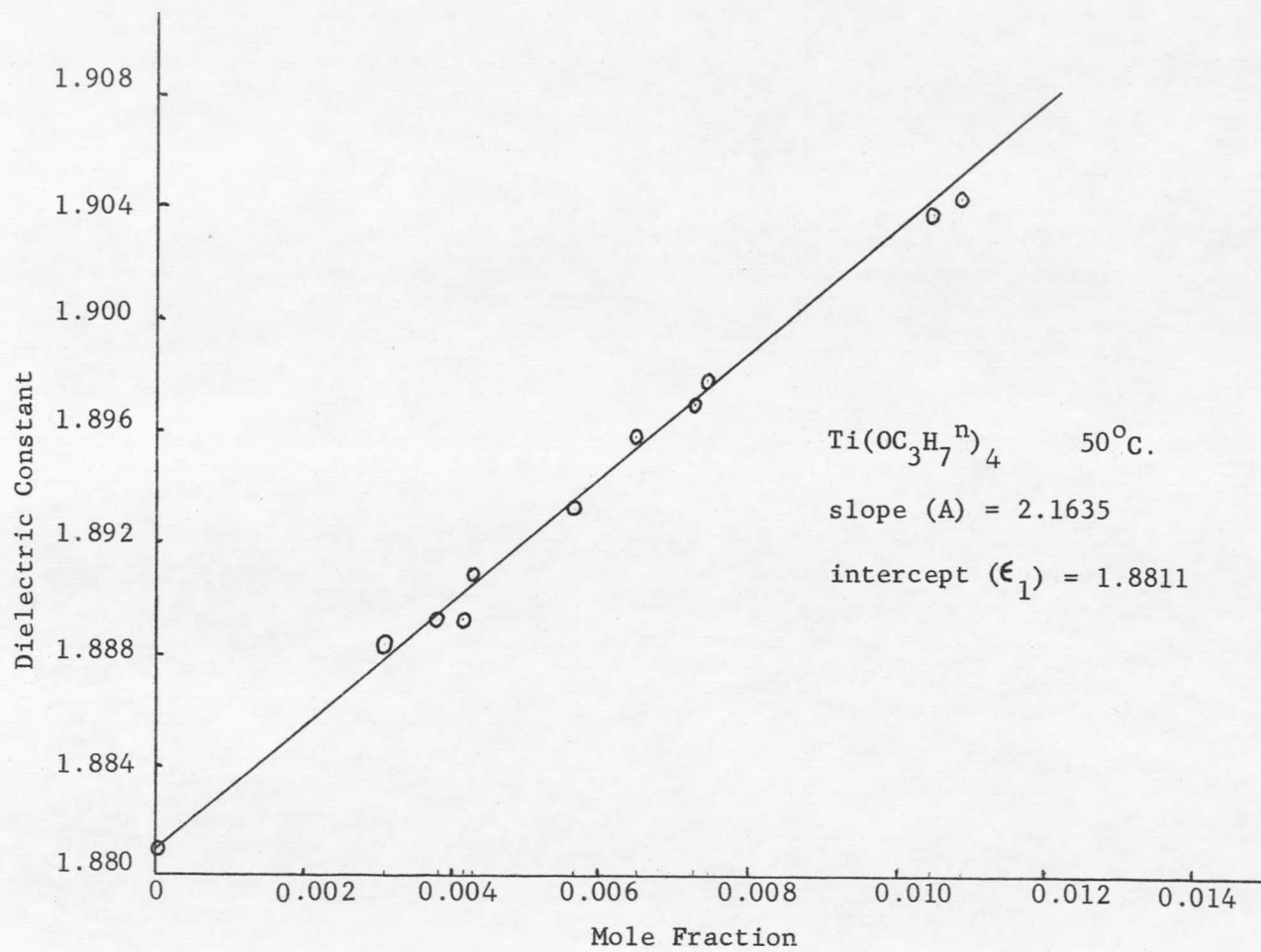
Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_2\text{H}_5)_4$, 50°C .

Figure 8



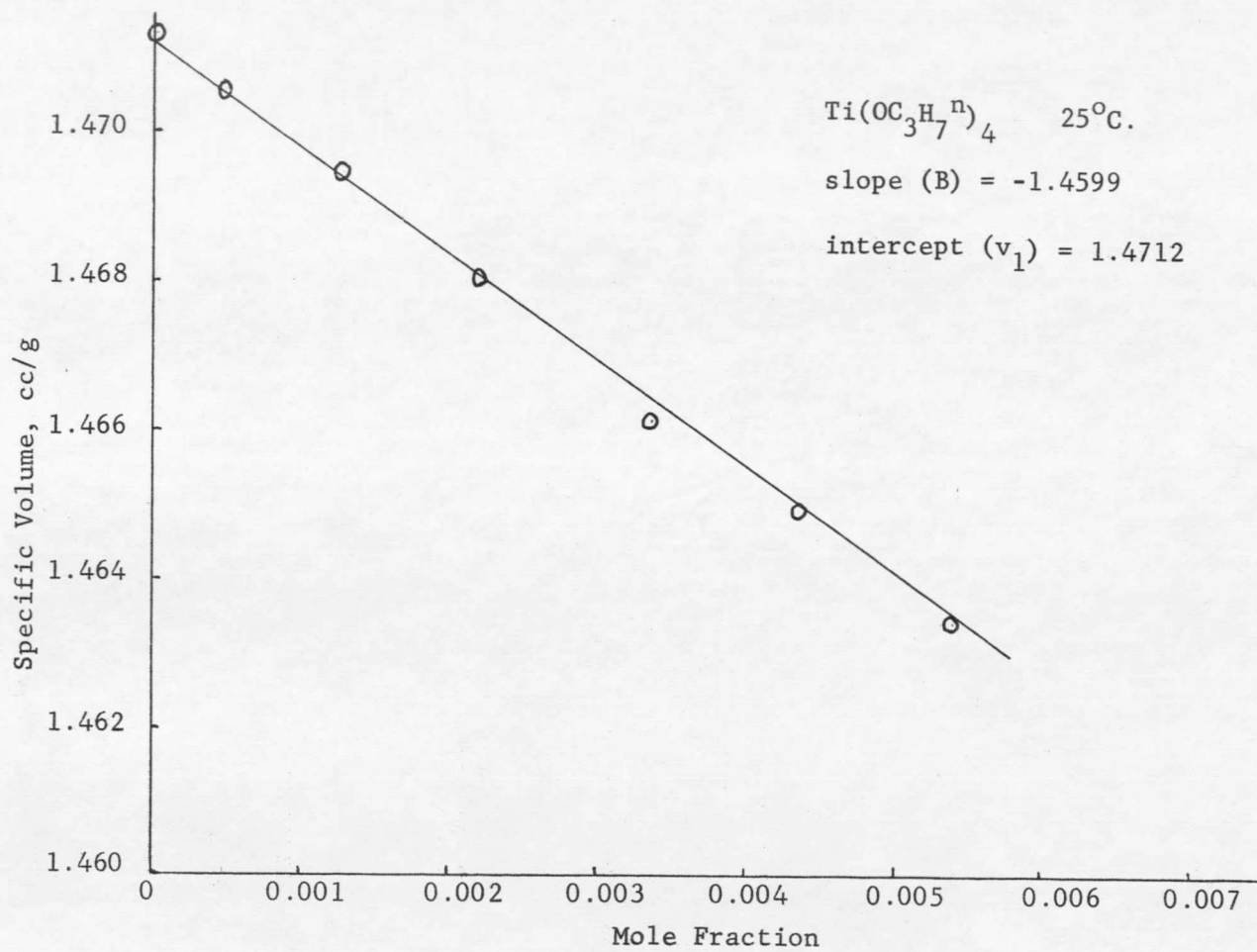
Specific Volume vs. Mole Fraction Curve for Ti(OC₃H₇ⁿ)₄, 50°C.

Figure 9



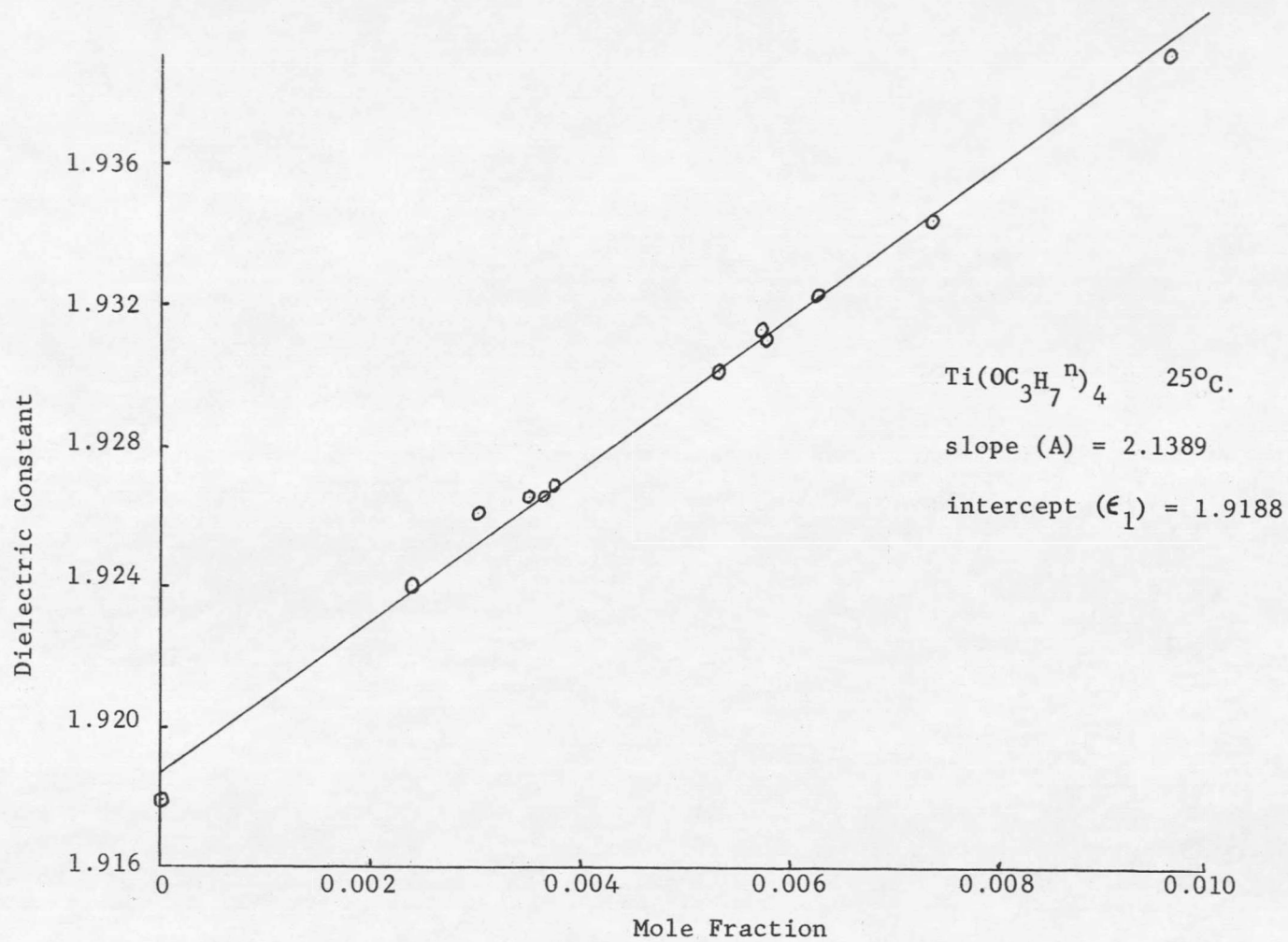
Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_3\text{H}_7^n)_4$, 50°C .

Figure 10



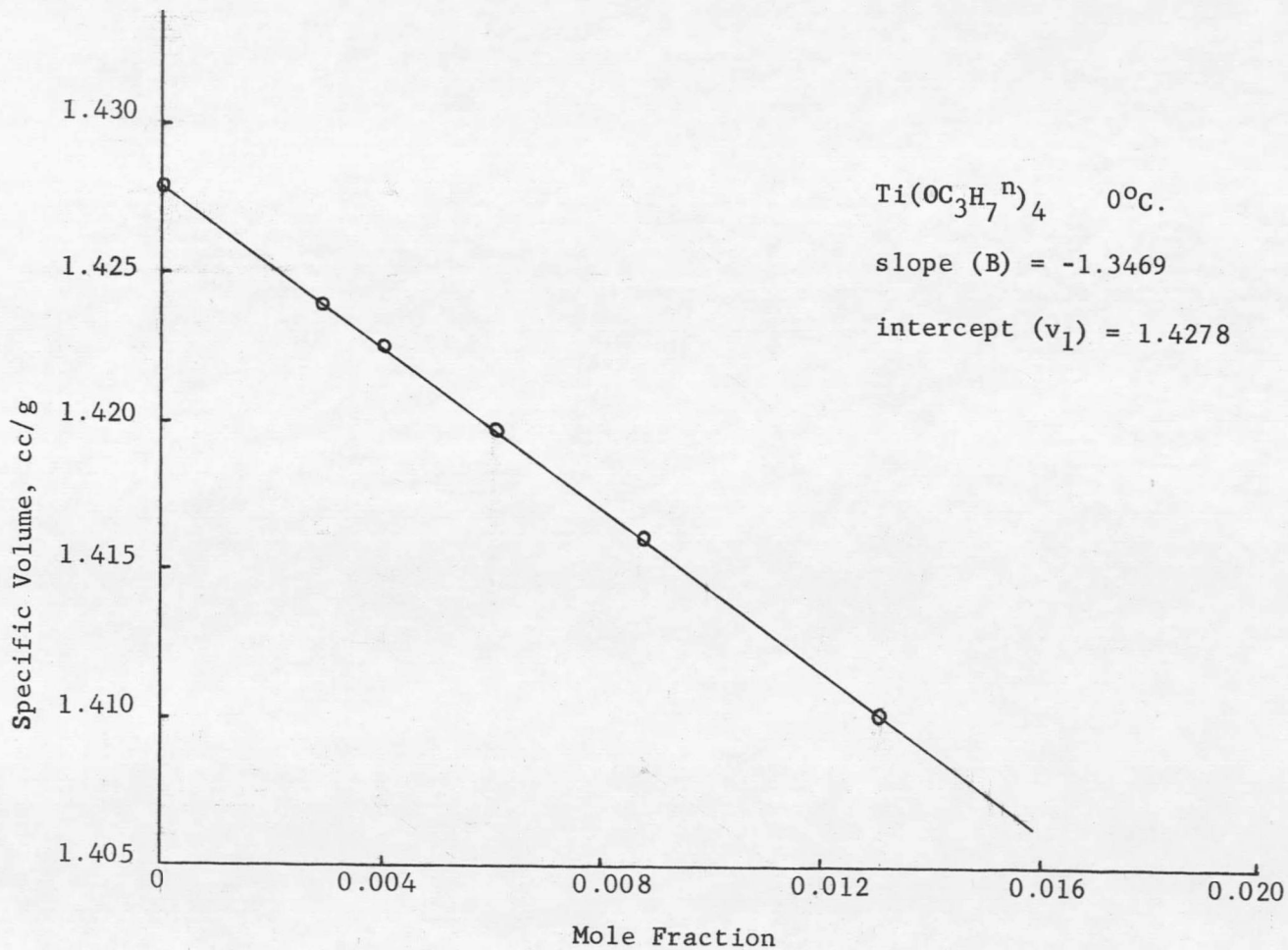
Specific Volume vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_3\text{H}_7^n)_4$, 25°C.

Figure 11



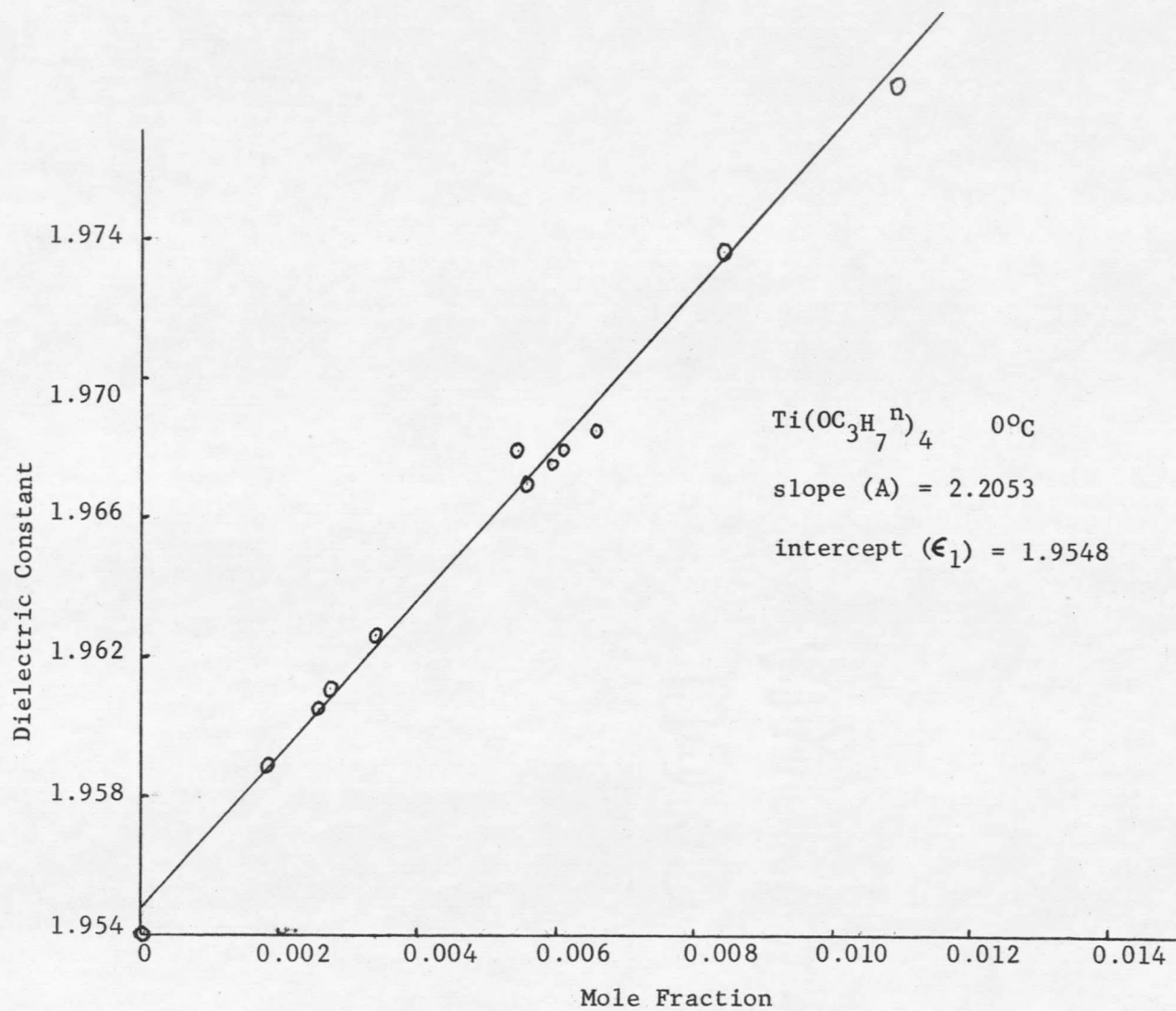
Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_3\text{H}_7^n)_4$, 25°C .

Figure 12



Specific Volume vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_3\text{H}_7^n)_4$, 0°C .

Figure 13



Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_3\text{H}_7^n)_4$, 0°C .

Figure 14

