



The electric moments and some other physical properties of VOCl_3 , VCl_4 and the simple alkyl orthovanadates
by Frederick Owen Cartan

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:

VOCl_3 , VCl_4 and several of the simple alkyl esters of orthovanadic acid have been prepared. Their densities, indices of refraction and dielectric constants have been measured. The alkyl esters were found to be monomeric in benzene. Solution values for the electric moments of these compounds were measured. The solvent for the alkyl orthovanadates was benzene; for the halides it was carbon tetrachloride. The electric moments of all compounds, except VCl_4 and t-butyl orthovanadate have been calculated using the Onsager equation. The observed solution electric moments and the Onsager moments are: (in debyes) Vanadium oxytrichloride ----0.31, 0.39; vanadium tetrachloride ---- 0, -- ; ethyl orthovanadate ----- 1.18,-1.16; n-propyl orthovanadate ---- 1.15, 1.11; i-propyl orthovanadate ---- 1.23, 1.40; n-butyl orthovanadate ---- 1.13, 1.09; i-butyl orthovanadate ----1.10, 1.10; s-butyl orthovanadate-----1.01, 1.30; t-butyl orthovanadate ---- 1.16,--- ; t-amyl orthovanadate ---- 1.11, 1.22.

These observed electric moments strongly indicate that the V-O bond moment is low. This can be explained by the assumption of pi bonding in this linkage. It is suggested that an equilibrium exists between the monomer and a polymer and that the color observed in several of the esters is due to the polymeric form.

Infrared, near infrared, visible and n.m.r. proton spectra are presented.

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OF VOCl_3 , VCl_4 AND THE SIMPLE ALKYL ORTHOVANADATES

BY

FREDERICK CARTAN

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at

Montana State College

Approved:

William B. Cook
Head, Major Department

Charles M. Caughlan
Chairman, Examining Committee

George Johnson
Dean, Graduate Division

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ABSTRACT

VOCl_3 , VCl_4 and several of the simple alkyl esters of orthovanadic acid have been prepared. Their densities, indices of refraction and dielectric constants have been measured. The alkyl esters were found to be monomeric in benzene. Solution values for the electric moments of these compounds were measured. The solvent for the alkyl orthovanadates was benzene; for the halides it was carbon tetrachloride. The electric moments of all compounds, except VCl_4 and t-butyl orthovanadate have been calculated using the Onsager equation. The observed solution electric moments and the Onsager moments are: (in debyes)

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INTRODUCTION

Vanadium tetrachloride (VCl_4) vanadium oxytrichloride (VOCl_3) and the alkyl orthovanadates (R_3VO_4) exhibit typical covalent properties. They possess low boiling points, low freezing points, negligible conductivity and are soluble in non-polar solvents. One would expect that these compounds should have low electric moments.

These vanadium compounds are infrequently prepared. Except for the halides, whose physical properties have received some study, little information on the electric moments of any of these compounds is available. This study was undertaken to determine the electric moments, some other physical properties and if possible, information on the structure of these interesting compounds.

In order to compute the electric moments, the total polarization and molar refraction of each of these substances must be measured. The former requires the determination of the dielectric constant and density of dilute solutions as a function of the concentration and, in addition, the measurement of the molecular weight in the same solvent. The latter requires the measurement of the index of refraction and density of each substance. Although not needed for the electric moment calculation, the dielectric constant of the pure substance along with other physical properties, can be used in the Onsager equation to calculate the approximate electric moment and thus provide a check on the value obtained from the solution measurements.

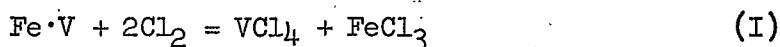
Inasmuch as only one other detailed study on the organic vanadates

has appeared, and that in 1913, it has been considered worthwhile to study the infrared, near infrared, visible and proton n.m.r. spectra of these substances. Although the present study of these spectra was not carried out in detail, the results are included as an aid to characterization and as a basis for further investigation.

Since these compounds are relatively unknown, short literature surveys, methods of preparation and descriptions are included here.

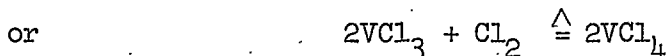
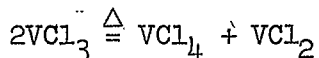
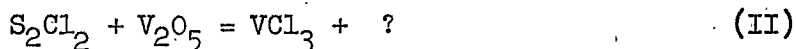
Vanadium tetrachloride (VCl_4) is an opaque red-black liquid which disproportionates slowly to VCl_3 and Cl_2 . Its dielectric constant³³, vapor pressure⁴⁵, b.p. and f.p.⁴⁶, density and magnetic susceptibility⁵⁰ have been studied.

Perhaps the most common method for the preparation of VCl_4 is that of Mertes³⁶. Ferrovandium is chlorinated directly at just under red heat.



The products, FeCl_3 and VCl_4 are separated by taking advantage of the relative insolubility of FeCl_3 in carbon tetrachloride.

A recent paper¹⁵ describes the preparation of VCl_4 by the following reaction sequence.



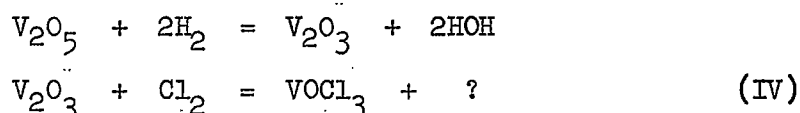
An additional method involving the use of a bomb reaction³⁰ is re-

ported to produce VCl_4 from CCl_4 and V_2O_5 . A sealed pyrex bomb at 400°C . is used.

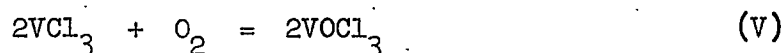


Vanadium oxytrichloride (VOCl_3) is a yellow mobile liquid boiling at 127°C . (760). Its vapor pressure²⁹, viscosity^{34,35} electronic spectrum³⁷, Raman and infrared spectra^{13,38}, melting point and heat of fusion¹⁷ and dielectric constant³³ have been studied.

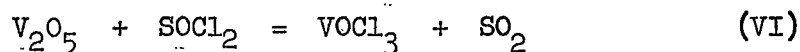
A number of methods are available for the preparation of this important vanadium halide. The most common preparation was developed by Prandl and Bleyer⁴³. The reaction sequence is as follows.



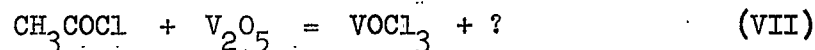
Improved purity of the product is claimed for a reaction involving the oxidation of vanadium trichloride²⁰.



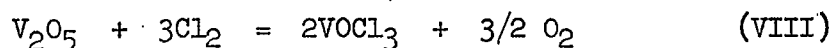
Two papers refer to the use of thionyl chloride, SOCl_2 , as a chlorinating agent for V_2O_5 ^{56,24}.



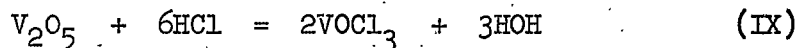
Vanadium oxytrichloride is produced using acetyl chloride as a chlorinating agent⁷.



The direct chlorination of V_2O_5 can be used to produce VOCl_3 . The same author has studied the kinetics of this reaction^{17,18}.

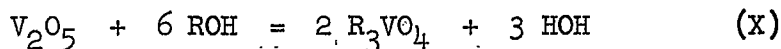


Another reaction involves the chlorination of V_2O_5 with gaseous HCl using phosphorus pentoxide as an agent for the removal of the water formed⁵⁵. Yields on this reaction are reported to be poor.

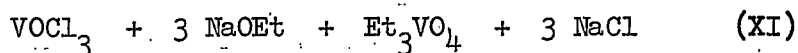


The lower alkyl esters of orthovanadic acid are yellow to colorless compounds, all liquids, except for the solid methyl and tertiary butyl esters. They hydrolyze rapidly, yielding first yellowish compounds and finally vanadium pentoxide as a reddish gel. Most of the esters will decompose above $150^\circ C$. or at lower temperatures if impure. Consequently, distillations must be conducted under low pressures.

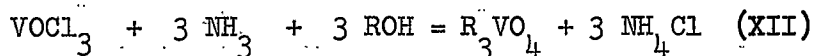
Several of these esters have been prepared previously. Hall²² in 1887 prepared the ethyl orthovanadate by the reaction of ethyl bromide and silver pyrovanadate. In 1913, Prandl and Hess⁴² prepared a number of these esters by the reaction of the corresponding alcohol with vanadium pentoxide.



Dr. Charles Caughlan, of this college, prepared the ethyl ester by the reaction between sodium ethoxide and vanadium oxytrichloride.

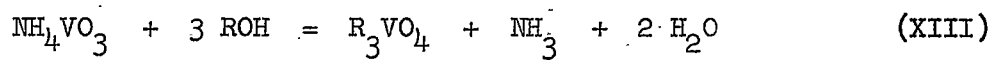


Other investigators^{56,19} have prepared the esters by the reaction of the corresponding alcohol with $VOCl_3$ and gaseous NH_3 .



It was found, as a part of this work, that the yields of reaction

X could be increased by the use of ammonium metavanadate in place of the vanadium pentoxide and by the use of an efficient fractionation column to separate the water-alcohol azeotrope.



EXPERIMENTAL

PREPARATIONS

Vanadium oxytrichloride

VOCl_3 was prepared by the method of Prandl and Bleyer⁴³. V_2O_5 mixed with kiesselguhr was reduced with H_2 at a red heat to form V_2O_3 . The apparatus was swept with N_2 gas to remove the last traces of H_2 and to prevent a possible H_2 - Cl_2 explosion and the V_2O_3 was chlorinated at a red heat to form VOCl_3 . The crude VOCl_3 was distilled several times. The pure VOCl_3 was obtained as a mobile yellow liquid boiling at $120.3(630\text{mm.})$.

VOCl_3 fumes strongly in moist air producing very irritating red-dish fumes. Unless the container is sealed, VOCl_3 will absorb moisture and become red colored. Ordinary drying procedures for laboratory glassware leave a film of adsorbed water which reacts with VOCl_3 vapor producing red films on the glass surfaces.

The troublesome character of VOCl_3 vapor merits notice. It will react with cork, rubber, stopcock grease and can freeze ground joints by formation of V_2O_5 upon contact with atmospheric moisture.

Vanadium Tetrachloride

Commercial ferrovanadium was broken into small pieces. The granules were loaded into a silica tube and the tube placed in an electric tube furnace. One end of the silica tube was arranged so that Cl_2 gas could be injected. The other end of the tube was connected to a large, water cooled distilling flask containing CCl_4 . Asbestos tape joints were used. The flow of chlorine was started and the furnace adjusted so that the tube maintained a dull red heat. A mixture of VCl_4 vapor and solid FeCl_3 was obtained. It was necessary to heat with a bunsen burner the portion of the silica tube outside the furnace to sublime the FeCl_3 into the carbon tetrachloride in order to prevent plugging of the combustion tube. At the conclusion of the preparation, the CCl_4 solution, containing the VCl_4 and the solid FeCl_3 , was distilled to separate the VCl_4 . The VCl_4 was stored as a CCl_4 solution and the VCl_4 was obtained by distillation when needed. Slow decomposition of the VCl_4 in the CCl_4 solution resulted in the loss of two batches when the resulting Cl_2 pressure loosened the stoppers.

Only material boiling above 140°C . at atmospheric pressure was used. VCl_4 is a reddish-black opaque liquid which produces white fumes in moist air and reacts with water to produce a blue solution containing VO^{++} ions.

Ethyl Orthovanadate

500 ml. of absolute alcohol were placed in a 1000 ml., 3-necked flask equipped with a mercury sealed stirrer, a reflux condenser and a dropping funnel. The flask and contents were cooled with an ice bath. 23 grams of Na were weighed out and added to the alcohol bit by bit. The reaction subsided in 2 hrs. The resulting solution of sodium ethylate was allowed to stand overnight. The solution was again chilled and approximately 28 ml. of VOCl_3 was added slowly with stirring. The reaction was violent. When the addition was complete the mixture was refluxed for 1/2 hour. The contents of the flask were then centrifuged to separate the NaCl. This supernatant liquid was distilled at atmospheric pressure until most of the alcohol was removed. The solution changed color (red-yellow) during the heating. Vacuum was applied, first without heating to remove some of the alcohol remaining, and then with heat. A red-orange distillate boiling at $85-89^\circ\text{C}$. (approximately 10 mm.) was collected. This product was redistilled, a cut boiling at $92-94^\circ\text{C}$. (13 mm.) was removed and the remaining liquid boiling at $94.5-96^\circ\text{C}$. (approximately 13 mm.) was collected. Some decomposition occurred during the distillation. The yield was approximately 80% of theoretical. The ethyl orthovanadate is a mobile yellow-orange liquid with a freezing point near 0°C .

N-Propyl Orthovanadate

600 ml. of n-propyl alcohol was fractionated using a 90 cm. glass helix packed column. A fraction boiling at 92°C . was taken. 25 grams of V_2O_5 was added to the alcohol and the resulting slurry was placed in the stillpot of the fractionating column. Boiling rate of the stillpot contents was kept rapid to reduce bumping. Distillate was removed from the top of the column when the temperature dropped below 91°C . When the mixture turned greenish, the excess n-propyl alcohol was removed at a low reflux ratio. When the volume remaining in the stillpot approached 50-100 ml., the stillpot contents were centrifuged and the orange supernatant liquid was placed in a vacuum distillation apparatus.

Excess n-propyl alcohol was removed with a water aspirator, the mixture being heated to 90°C . A mechanical vacuum pump was connected and the n-propyl ester was distilled over at $79-89^{\circ}\text{C}$. (~ 1 mm) (depending on the stillpot temperature). The yield was about 50%.

A second preparation was made using NH_4VO_3 in place of V_2O_5 . A purple color was observed in the slurry after heating. The yield was similar.

n-propyl orthovanadate is a lemon yellow liquid. Like the other esters, it hydrolyzes rapidly on contact with moisture.

Isopropyl Orthovanadate

600 ml. of Eastman 98-99% isopropyl alcohol were fractionated with a 90 cm. glass-helix packed column. The first 100 ml. of distillate were rejected and a constant boiling fraction collected. Approximately 20 grams of V_2O_5 (prepared by heating NH_4VO_3 to $200^{\circ}C.$) was added. The slurry was allowed to reflux on the column occasionally taking off distillate at a 25:1 ratio until the column head temperature approached that of boiling pure isopropyl alcohol. When the mixture turned green the excess isopropanol was taken off. When the stillpot volume approached 100 ml. the stillpot contents were centrifuged and the clear supernatant liquid transferred to a vacuum still. Isopropyl alcohol was removed with warming under water aspirator vacuum. A mechanical vacuum pump was attached. The isopropyl ester was distilled at a temperature of $60-70^{\circ}C.$ under pump vacuum ($\sim 1mm$). The product was a clear colorless mobile liquid. The yield was 60-70%.

N-Butyl Orthovanadate

500 ml. of Eastman Practical grade n-butyl alcohol was purified by fractionation through a 90 cm. glass helix packed column and was placed in the stillpot of the column. 40 grams of NH_4VO_3 was added in 10 gram increments over a period of two hours. The mixture was refluxed for approximately six hours, distillate being removed at high reflux ratio until the condensation temperature rose to within 5° of that of the pure alcohol. The excess n-butyl alcohol was removed at a low reflux

ratio until the stillpot temperature reached 130°C . The stillpot contents were centrifuged and the clear orange yellow supernatant liquid transferred to a vacuum still.

The n-butyl ester was obtained as a clear yellow liquid boiling at $100-110^{\circ}\text{C}$. under pump vacuum. Approximately 80 ml. (90% yield) was obtained.

Isobutyl Orthovanadate

500 ml. of Eastman white label isobutyl alcohol were fractionated through a 90 cm. glass-helix packed column. The fraction boiling at 102° (639 mm.) was placed in the stillpot. 40 grams of NH_4VO_3 were added. The slurry was refluxed for approximately 8 hours, with removal of distillate whenever the condensation temperature dropped below 95°C . The remaining alcohol was taken off at a 2:1 reflux ratio until the stillpot temperature reached $125-130^{\circ}\text{C}$. The contents of the stillpot were purple. The stillpot contents were centrifuged and the supernatant liquid transferred to a vacuum still. The excess alcohol was removed by a water aspirator at 70°C . A mechanical vacuum pump was attached and the iso-butyl ester taken off as a pale yellow liquid.

The yield was 50-60 ml. (60% yield).

Sec-Butyl Orthovanadate

600 ml. of sec-butyl alcohol were obtained and fractionated through a 90 cm. glass helix packed column. The fraction boiling at 94.5--95.0°C was collected. 50 grams of NH_4VO_3 were added and the resulting slurry placed in the stillpot of the column. The mixture was brought to a violent boil and distillate was removed whenever the condensation temperature exceeded 90°C. When the condensation temperature remained constant, the excess alcohol was removed at a 2:1 reflux ratio until the stillpot temperature reached 115°C. The contents of the stillpot were centrifuged and the yellowish supernatant liquid transferred to a vacuum still. The excess alcohol was removed by gentle heating under water aspirator vacuum. The mechanical vacuum pump was then attached and the ester was obtained as a clear colorless liquid boiling at 75-78°C. (71 mm). The yield was approximately 60%. This compound froze at a temperature a few degrees below 0°C..

Tertiary Butyl Orthovanadate

Small amounts of tertiary-butyl orthovanadate have been prepared by the method used for the other esters. The high freezing point of t-butyl alcohol can cause plugging of the reflux condenser. Yields were very low, only 10-12 grams of the ester being obtained from 40 grams of NH_4VO_3 . t-butyl orthovanadate is a colorless solid. Its melting point is near 45°C.

Tertiary Amyl Orthovanadate

800 ml. of Eastman t-amyl alcohol were fractionated through a 90 cm. column. A 600 ml. fraction boiling at 96°C . (640 mm.) was taken. 40 grams of V_2O_5 prepared by heating NH_4VO_3 to 200°C . were added and the slurry was placed in the stillpot of the 90 cm. column. The tertiary amyl alcohol-water azeotrope was removed by distillation whenever the condensation temperature dropped below 95°C . When a constant temperature was reached the excess tertiary amyl alcohol was removed at low reflux ratio. The stillpot temperature was accidentally allowed to reach 150°C . The contents were removed and centrifuged. The supernatant liquid was transferred to a vacuum still and the excess t-amyl alcohol remaining was removed by gentle warming under water aspirator vacuum. The mechanical vacuum pump was connected and the t-amyl ester obtained in good yield as a clear colorless liquid boiling near 140° (41 mm) 90 ml. were obtained. The stillpot should not be allowed to reach 150°C for this preparation as decomposition may set in above 130°C .

ANALYSES

Method

Vanadium was determined by a titration of the VO^{++} ion with permanganate ion, which acted as both oxidant and indicator. Vanadium (V) compounds were decomposed by fuming H_2SO_4 and reduced to VO^{++} with SO_2 . The VO^{++} ion was titrated while hot. A nitrogen sweep was used during heating to prevent oxidation of VO^{++} by atmospheric oxygen. A blank was carried through the procedure. The precision of the method was 0.36% for duplicate determinations at the 95% confidence limits.

Procedure

The samples of the vanadium compound was weighed into 250 ml. Erlenmeyer flasks containing 10 ml. of water and 5 ml. of concentrated H_2SO_4 . The flasks were heated until strong fumes of SO_3 appeared. The flasks were allowed to cool and 75 ml. of water and 3 ml. of conc. H_2SO_4 was added to each flask. Excess Na_2SO_3 was added to the flasks and they were allowed to stand overnight to allow complete reduction. A flask was then fitted with a nitrogen sweep and heated to boiling, still maintaining the nitrogen sweep. After boiling five minutes, the contents of the flask were titrated, while still hot, with standard KMnO_4 . There was an excellent anticipatory color change (blue-green-yellow) at the endpoint. Blanks were given identical treatment. The titration could be repeated once or twice by rereducing the vanadium with Na_2SO_3 , adding additional H_2SO_4 if needed.

TABLE I

Summary of analytical results

compound	% vanadium	
	<u>theoretical</u>	<u>found</u>
vanadium oxytrichloride	29.39	29.31
vanadium tetrachloride	26.43	26.43
ethyl orthovanadate	25.21	25.25
n-propyl orthovanadate	20.86	20.65
i-propyl orthovanadate	20.86	20.84
n-butyl orthovanadate	17.80	17.82
i-butyl orthovanadate	17.80	17.74
s-butyl orthovanadate	17.80	17.76
t-amyl orthovanadate	15.52	15.61

SPECTRA

Nuclear magnetic resonance proton spectra

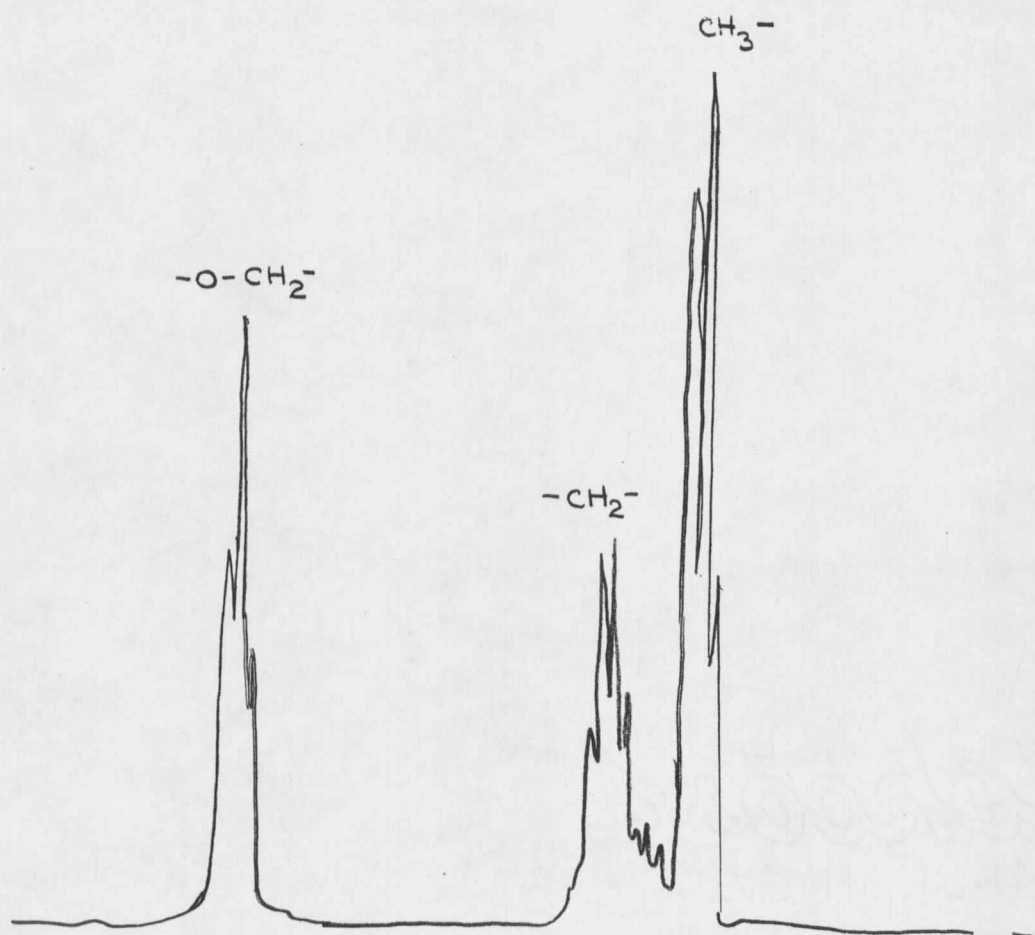
The following n.m.r. proton spectra of several of the esters of orthovanadic acid were obtained Sept. 29, 1958 with the 60 mc. Varian High Resolution instrument of the University of Washington.

The esters were vacuum distilled into selected 5 mm pyrex tubing. The tubes were sealed off under vacuum. A series of solutions of the n-propyl ester and the t-amyl ester of varying concentration in CCl_4 was prepared. The tube containing the ethyl ester showed evidence of decomposition and was not examined.

The spectra, Figures 1-7, show only the expected features of the alkyl group of the esters examined⁴⁵. There was no shift of the O-CH peak upon dilution. The CH_3 peak was considered as the reference since it would not be likely to be influenced by the possible existence of hydrogen bonding. These spectra indicate only that the proper alcohols were used for the preparation and that isomerization of the alkyl group has not occurred.

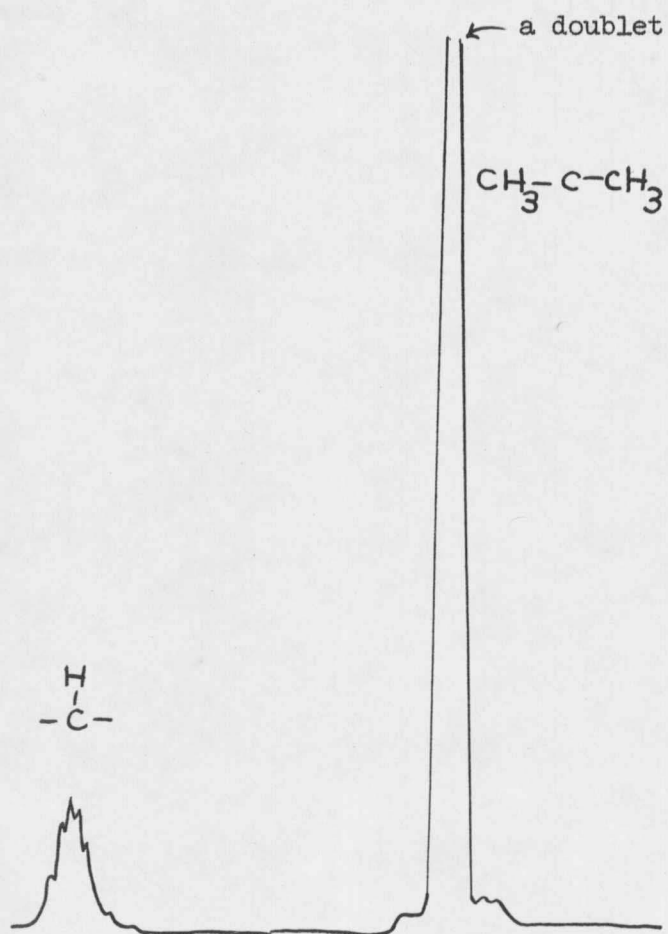
Experimental

spin rate 600 rpm
H 14,100 gauss
frequency 60 mc.
sweep field 25-200 milligauss
sweep freq. 60 cps.



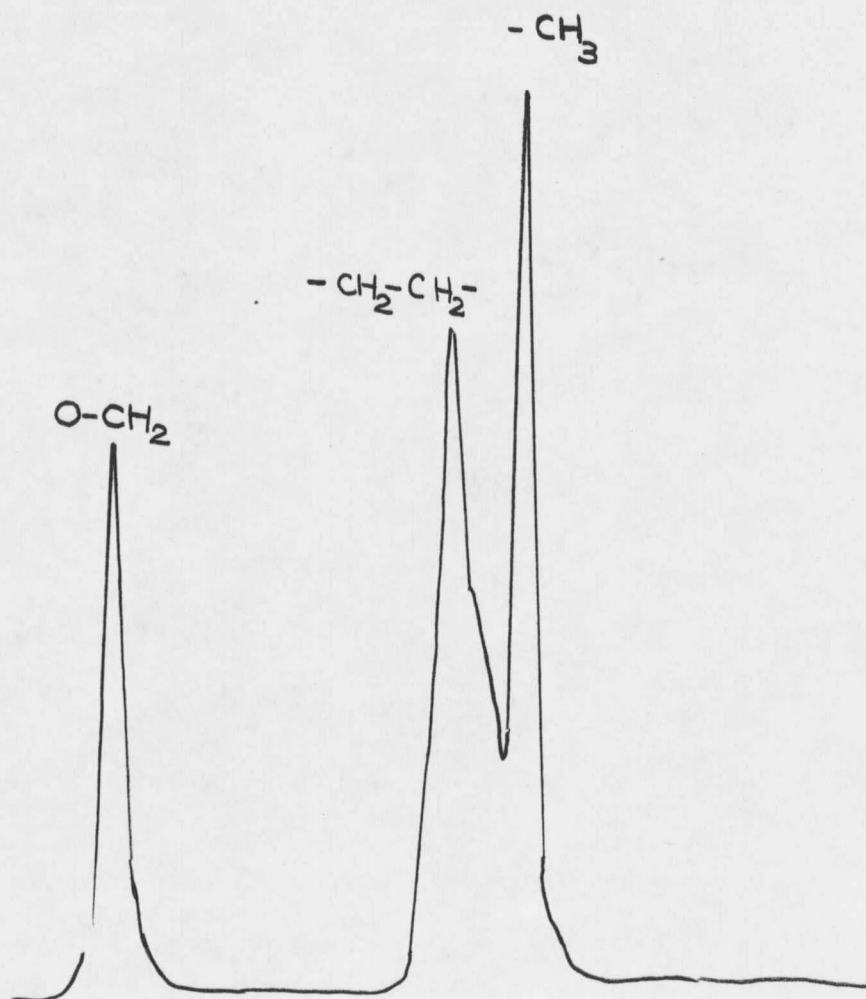
proton n.m.r. spectra of n-propyl orthovanadate

Figure 1



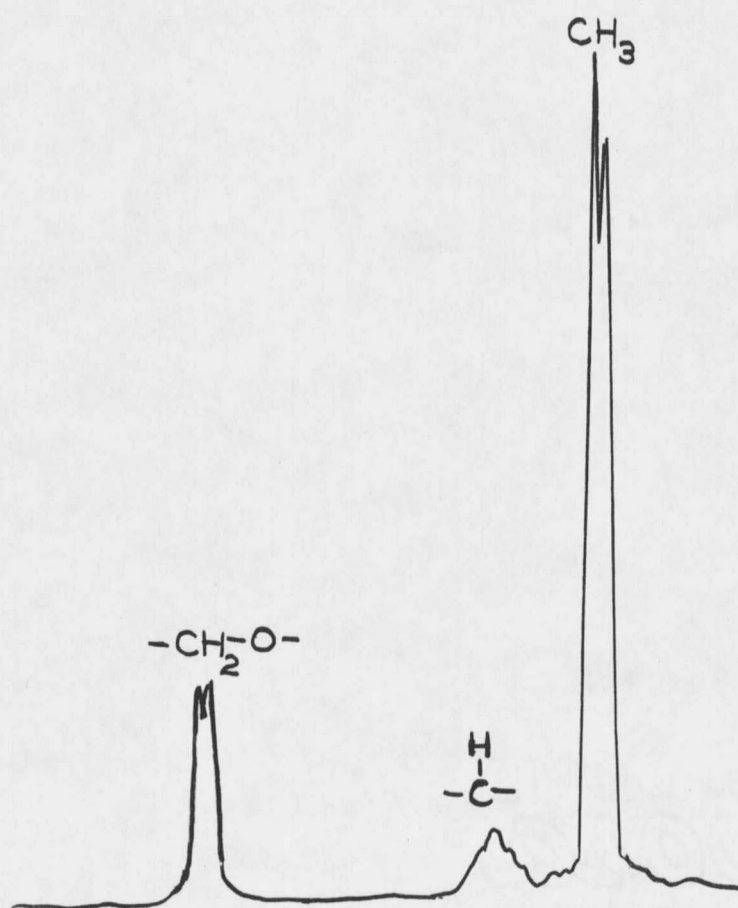
proton n.m.r. spectra of iso-propyl orthovanadate

Figure 2



proton n.m.r. spectra of n-butyl orthovanadate

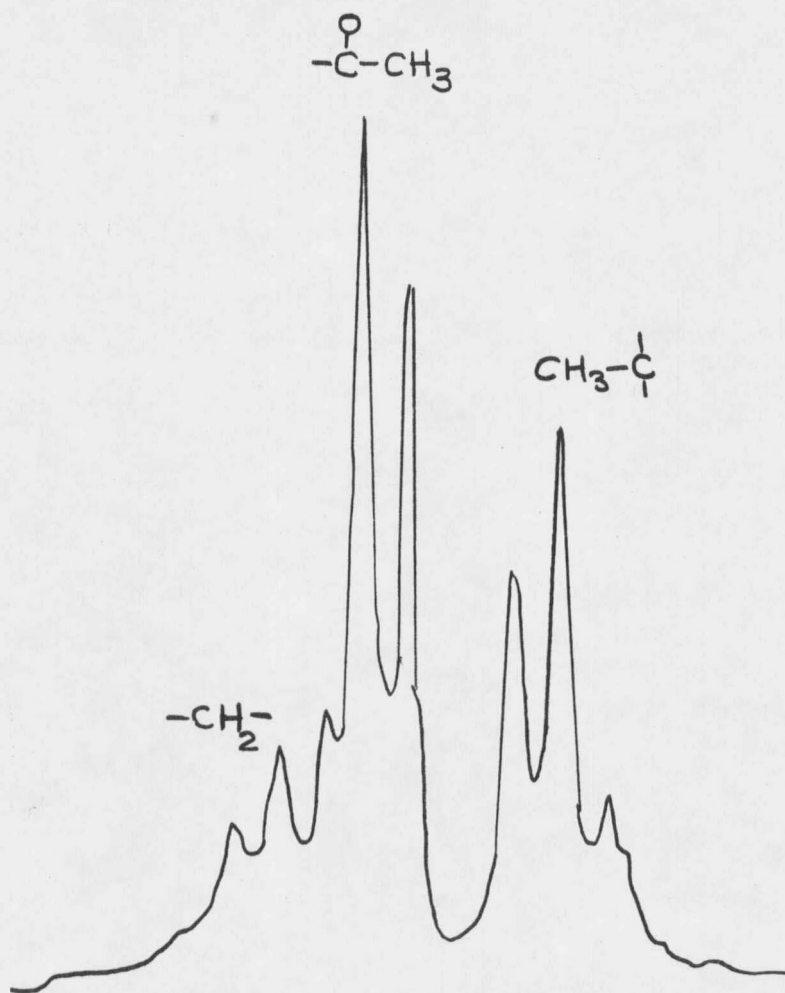
Figure 3



proton n.m.r. spectra of iso-butyl orthovanadate

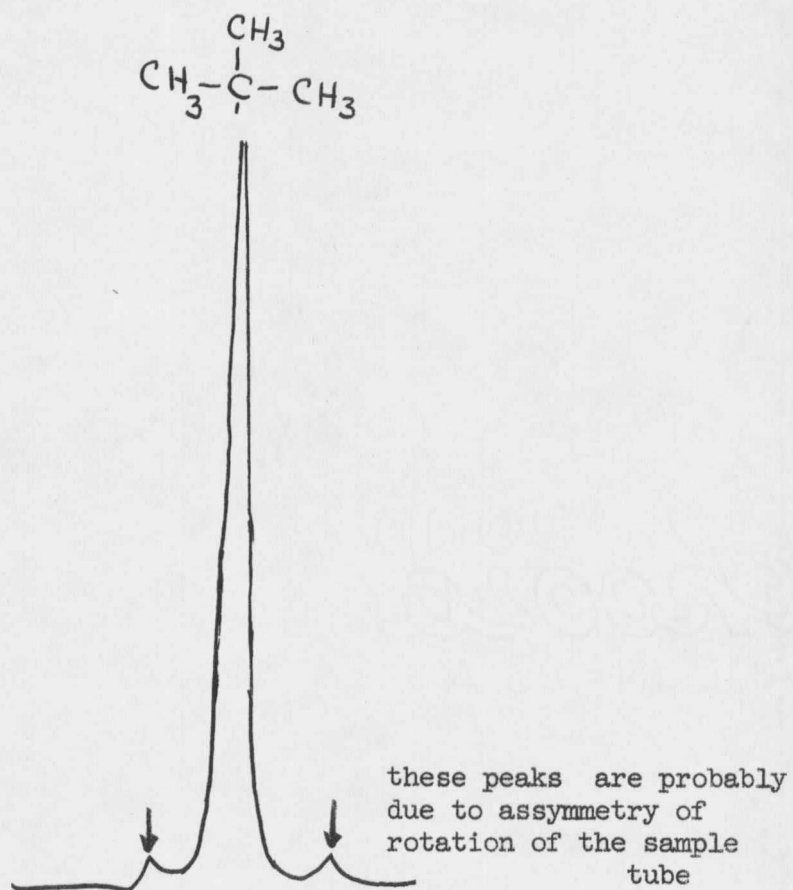
Figure 4

The $\begin{array}{c} \text{H} \\ | \\ -\text{C}- \\ | \end{array}$ peak is missing. Chamberlain⁶ reports that this peak in sec-butyl alcohol is weak and shows no structure.



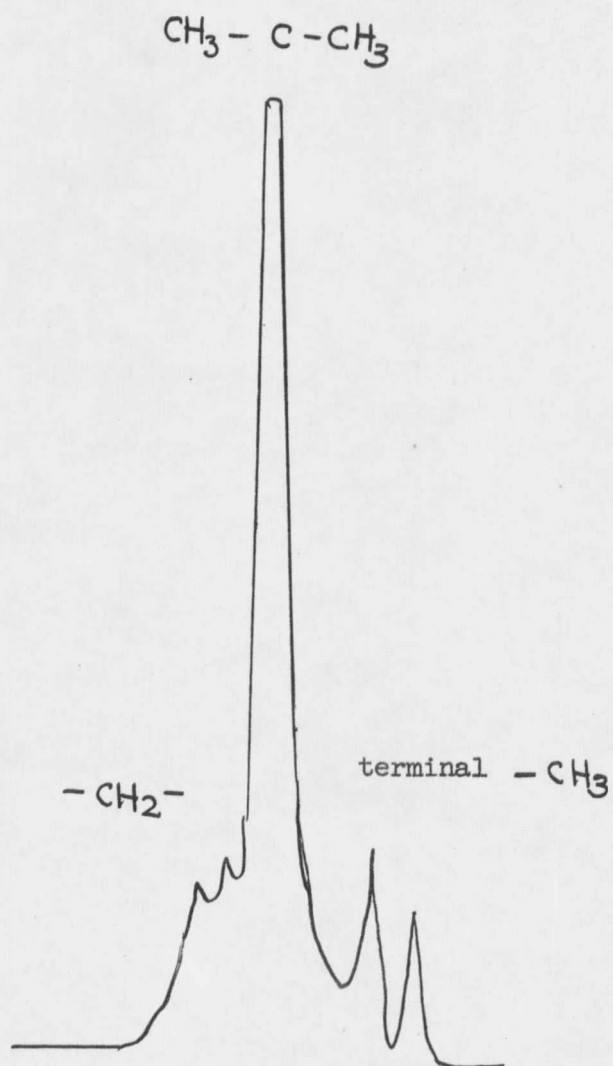
proton n.m.r. spectra of sec-butyl orthovanadate

Figure 5



proton n.m.r. spectra of a CCl_4 solution of t-butyl ortho-
vanadate

Figure 6



proton n.m.r. spectra of tert-amyl orthovanadate

Figure 7

Visible and near infrared spectra

The absorption spectra reproduced here and in the discussion section of this thesis were obtained with the Beckman DK-2 Ratio Recording Spectrophotometer. One cm. quartz cells with loosely fitting caps were used for the measurements.

The compounds appeared to have identical spectra. Each spectrum shows weak peaks at 1200 $\text{m}\mu$ and 1400 $\text{m}\mu$, peaks of medium intensity, with considerable structure, at 1700-1800 $\text{m}\mu$ and strong peaks near 2300, 2470 and 2570 $\text{m}\mu$. There is strong absorption in the ultraviolet resulting in a cutoff at the vicinity of 350 $\text{m}\mu$.

Spectra shown in this section were taken in dilute CCl_4 solution with a CCl_4 reference.

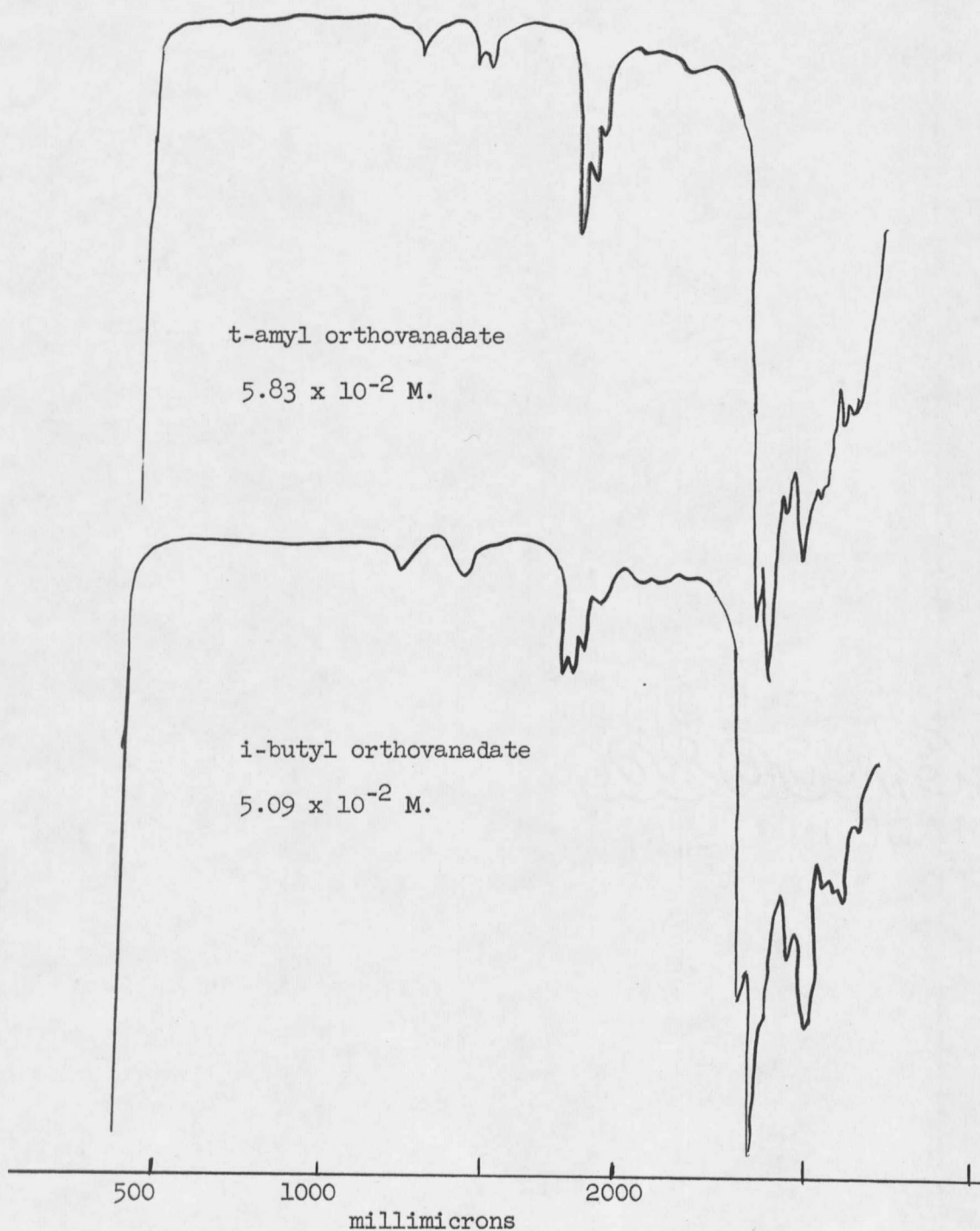
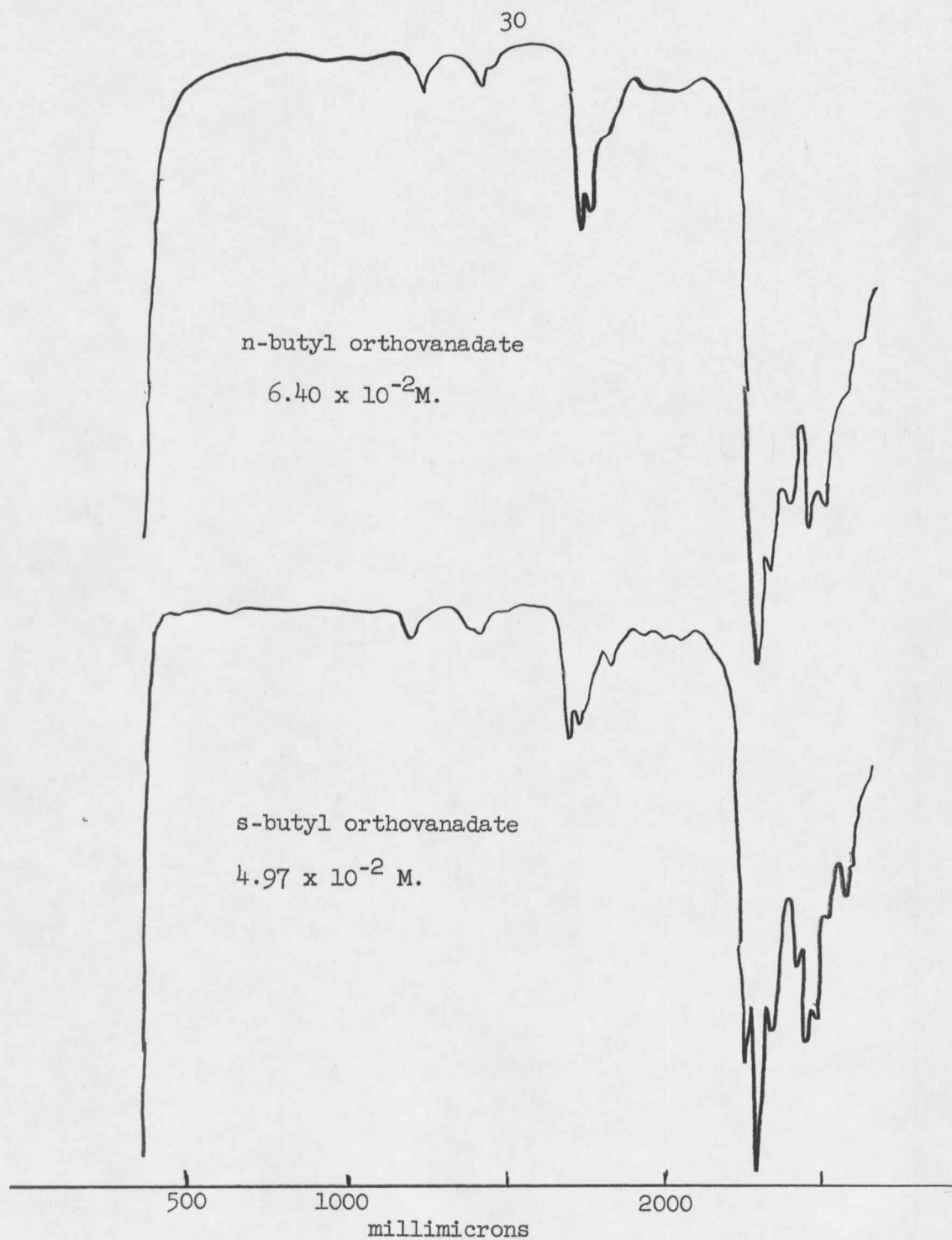
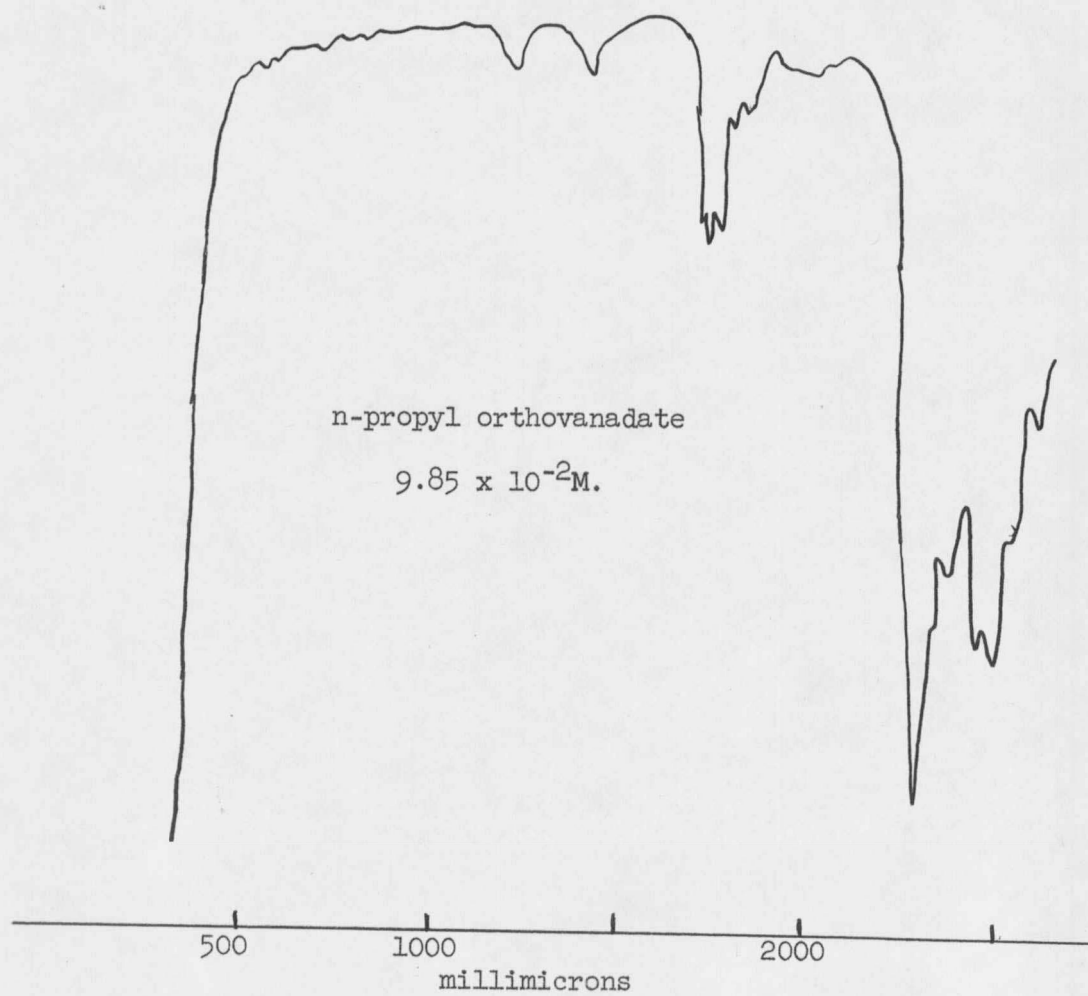


Figure 8 -- visible and near IR spectra of the alkyl orthovanadates



Visible and near IR absorption spectra of the alkyl orthovanadates

Figure 9



Visible and near IR absorption spectra of the alkyl
Orthovanadates

Figure 10

Infrared spectra

Infrared spectra of the pure esters were taken with the Beckman IR-4 Recording IR spectrophotometer. This instrument records linearly with respect to wave numbers. These spectra are reproduced in Figures 11, 12, 13.

The spectra shown here were taken with a capillary film between NaCl plates. An air reference was used. The spectra shown have been reduced $3 \frac{1}{2}$ times resulting in the loss of some resolution. The original spectra are on file.

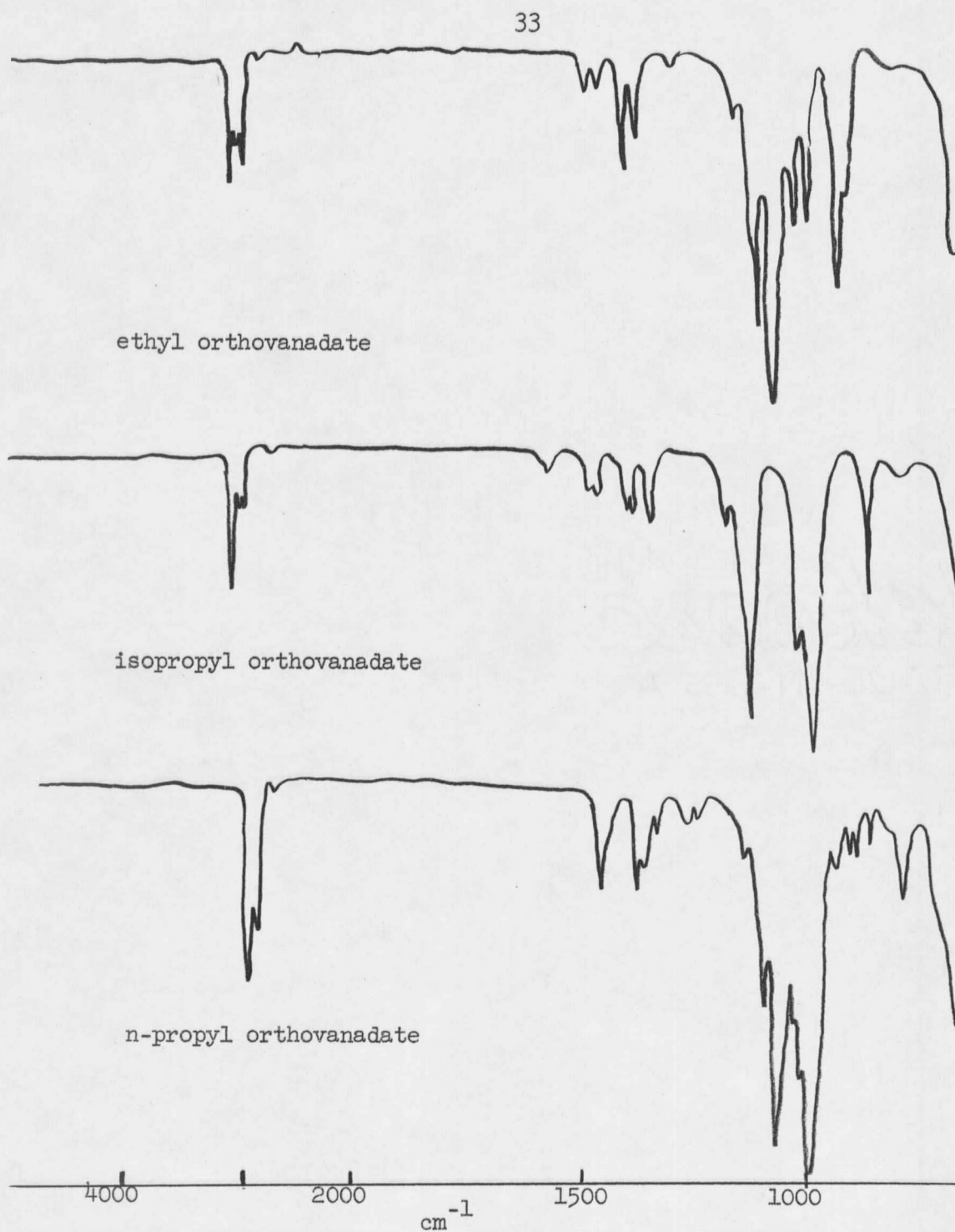


Figure 11 --- Infrared absorption spectra of the alkyl orthovanadates

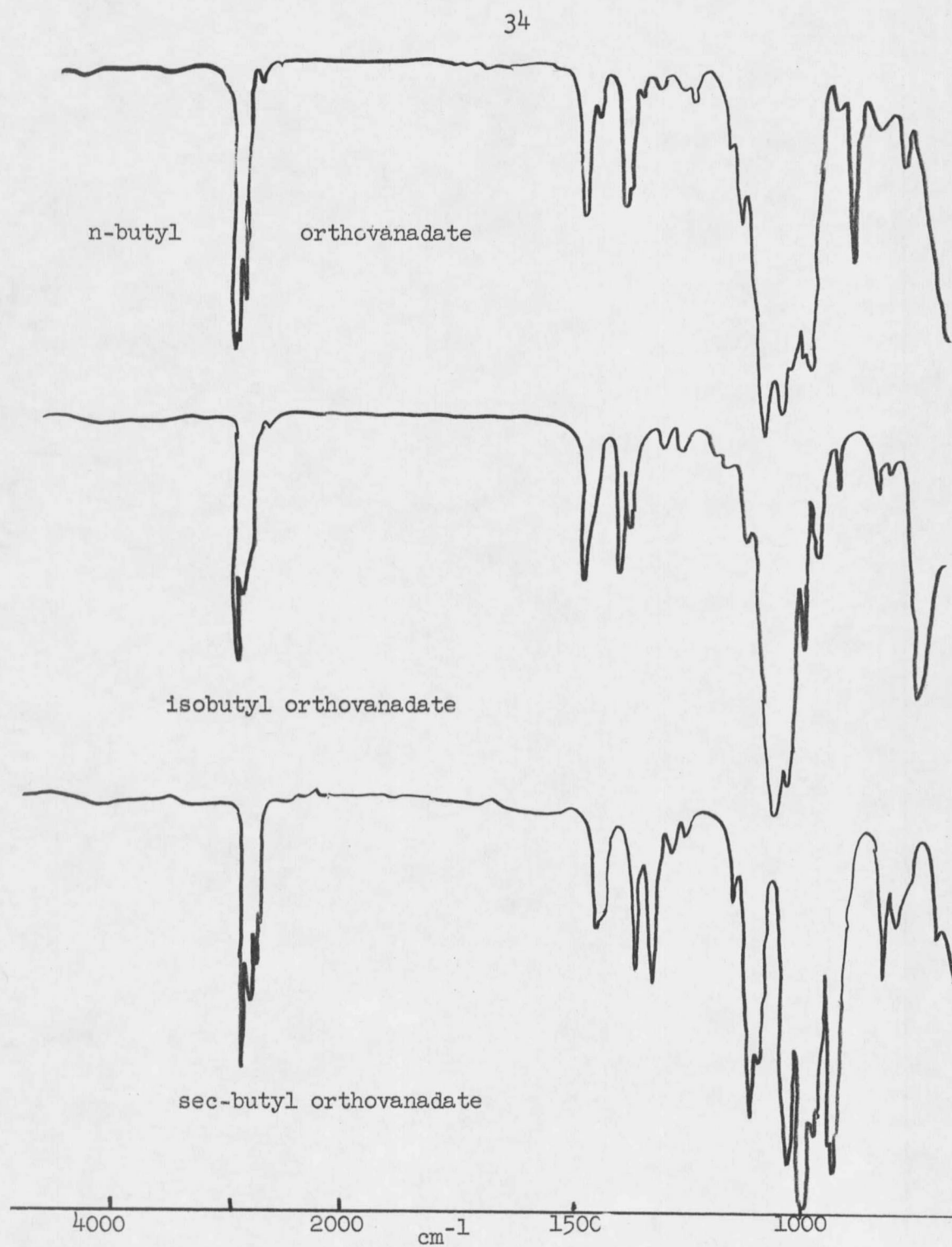


Figure 12 ---- Infrared absorption spectra of the alkyl orthovanadates

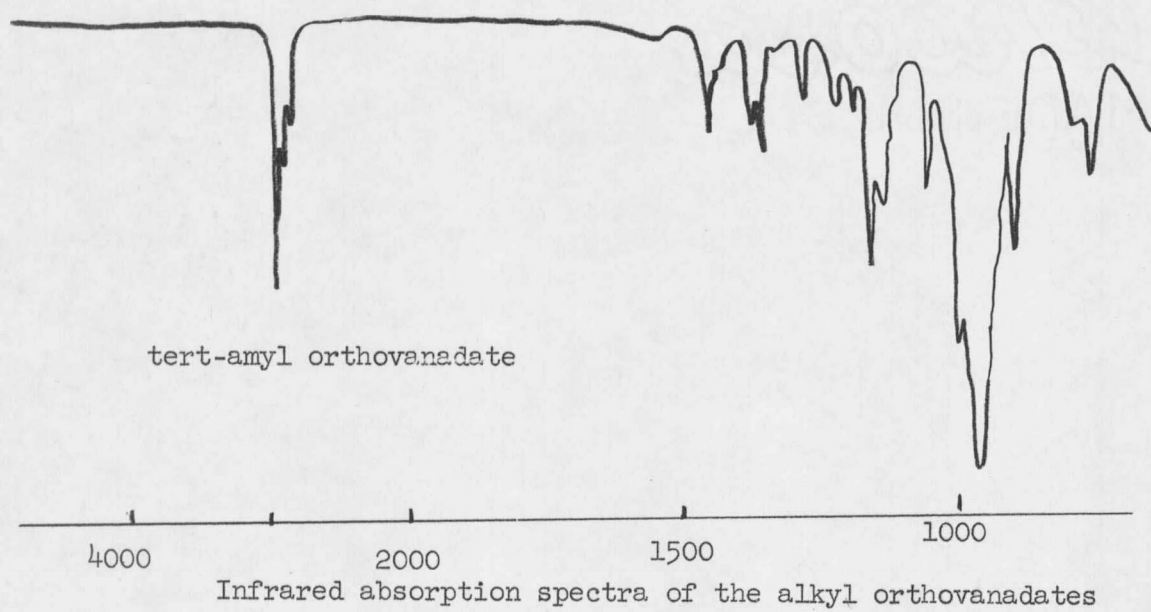


Figure 13

PHYSICAL PROPERTIES OF THE PURE LIQUIDS

Densities

The contents of the stock bottles were purified by a double vacuum distillation. A large middle fraction was collected.

The densities were determined with a simple pycnometer of the single neck capillary bore type. The capillary bore diameter was 2 mm. and the volume of the pycnometer was approximately 30 ml. The flask was filled with a 20 cc hypodermic syringe and a 6" #18 needle. Final adjustment to the etched ring was done using a medicine dropper drawn to a long fine tip. The pycnometer was immersed in a thermostat at 24.7°C.

The pycnometer was calibrated with distilled water. No corrections were made for vapor in the air space or for dissolved gases since both these were considered small or negligible. All weights were corrected to vacuum values. A duplicate pycnometer was used as a tare. The density of air at the local altitude was taken as 1.0 g/liter. (630-640 mm.). Weights used were checked against a NBS certified reference set. The balance had a sensibility of 0.05 mg and no difference in the beam arms could be detected.

The most likely sources of error were: 1) variation in the adjusted level; 2) droplets of the esters or their hydrolysis products on the walls of the capillary, the expansion chamber or the ground joint.

It is felt that the measured density values of the liquids are correct to the 4th decimal place.

The observed densities of the compounds studies are listed in Table II. The corresponding literature values are given when available.

TABLE II
Densities of the Vanadium compounds

compound	T(° C)	d_4^{25}	Lit. values	Ref.
VOCl_3	25	-----	1.8203	(26)
VCl_4	25	-----	1.8198	(59)
Et_3VO_4	24.7	1.1550	1.167(17.5°) 1.167(20°) 1.167(15°)	(22) (56) (42)
Pr_3VO_4	24.7	1.0752	1.088(15°)	(42)
Pr_3^iVO_4	24.7	1.0324		
Bu_3^nVO_4	24.7	1.0335	1.031(20°) 1.037(20°)	(56) (40)
Bu_3VO_4	24.7	1.0189	1.033(15°)	(42)
Bu_3^sVO_4	24.7	1.0083		
Am_3^tVO_4	24.7	0.9863		

Refractive Indices

The refractive indices of VOCl_3 and the pure esters were measured with a Zeiss Abbe refractometer. The temperature was controlled with circulating water from a 25°C thermostat.

This instrument can be read directly to 0.001 and estimated to 0.0001 units of refractive index. It was calibrated with distilled water. The measured refractive indices are considered accurate to ± 0.0004 .

The refractive indices of the esters were measured after two vacuum distillations. Samples left between the refractometer prisms for periods of 15 minutes showed little change in apparent refractive index, indicating that hydrolysis of the ester was not an important source of error. VOCl_3 was introduced between the prisms with a fine tipped micropipette. The method cannot be recommended for this compound since the instrument required partial disassembly for cleaning after this use. Duplicate measurements on VOCl_3 were consistent, but some hydrolysis of this volatile liquid was likely.

The measured refractive indices of these liquids are given on the following table. Such literature values as exist are included.

TABLE III

Measured Refractive Indices.

Compound	n_D^{25}	lit. values
VOCl_3	1.630	
Et_3VO_4	1.5059	$n_D^{20} = 1.5103$
$\text{Pr}_3^{\text{n}}\text{VO}_4$	1.4953	
$\text{Pr}_3^{\text{i}}\text{VO}_4$	1.478	
$\text{Bu}_3^{\text{n}}\text{VO}_4$	1.4898	$n_D^{20} = 1.4898$
$\text{Bu}_3^{\text{i}}\text{VO}_4$	1.4857	
$\text{Bu}_3^{\text{s}}\text{VO}_4$	1.4804	
$\text{Am}_3^{\text{t}}\text{VO}_4$	1.4805	

Dielectric constants

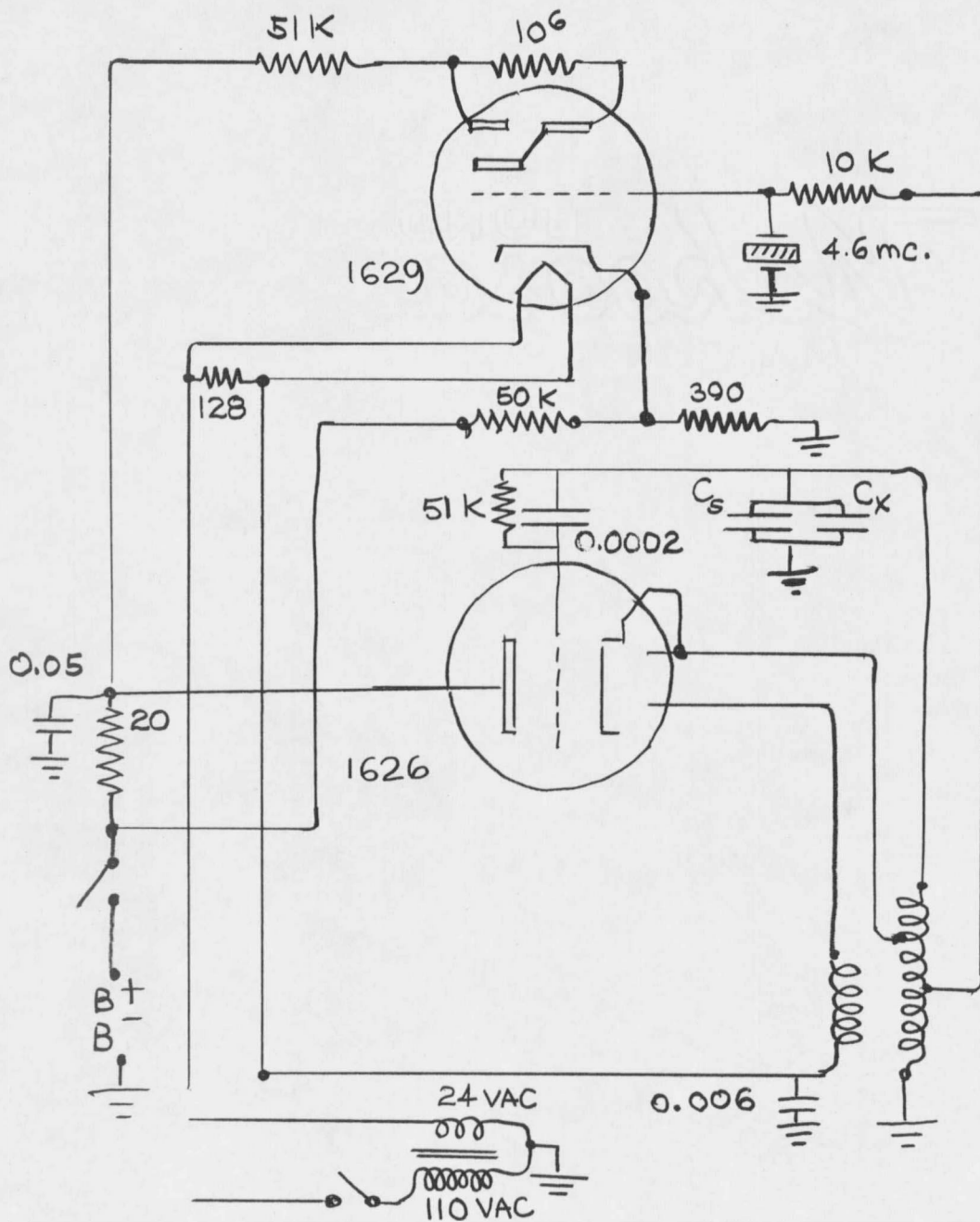
The apparatus described is an adaptation of a circuit described by Alexander¹ and used by Caughlan and Crowe¹⁰. The circuit for the apparatus is shown as Figure 14. When the resonant frequency of the circuit containing the cell and precision condenser matches the circuit containing the crystal, the "electric eye" opens. The frequency used was 4.6 mc. The precision condenser was a General Radio 722-D Standard Precision Condenser.

The cell of the dielectric constant apparatus consisted of three concentric platinum cylinders in a glass container. The inner and outer cylinders were spot welded together and the arrangement had a capacitance of approximately 25 μpfd . The container was jacketed to allow circulation of water from a thermostat for temperature control. Leads from the cylinder were sealed through the glass container and soldered to two banana plugs with the proper spacing for the jacks of the Standard Precision condenser.

The cell constant (capacitance) was measured using benzene and cyclohexane as standard liquids. Both liquids were dried by distillation from metallic sodium. The following values were used as the dielectric constants of benzene and cyclohexane at 25°C.²⁶

$$\frac{\epsilon}{\epsilon_v} \text{ (benzene)} = 2.274 \quad \frac{\epsilon}{\epsilon_v} \text{ (cyclohexane)} = 2.015$$

The exact cell constant was 24.65 μpfd .



Circuit of dielectric constant apparatus

Figure 14

The esters were vacuum distilled twice before measurement of the dielectric constants. After the apparatus had stabilized, the reading of the precision condenser with the cell containing dry air was recorded. The ester or other liquid was then poured into the cell and the reading of the precision condenser again recorded. The cell was emptied, cleaned with acetone and cleaning solution, washed, dried and the reading of the precision condenser with dry air in the cell taken for the second time. The difference between the average reading of the air-filled cell and the reading with the cell filled with the ester or other liquid was used to compute the dielectric constant of the liquid.

VOCl_3 and VCl_4 were distilled only once just before their introduction into the cell, otherwise the procedure was the same.

The following equation was used to compute the dielectric constants.

$$= \frac{C_{\text{air}} - C_x}{24.65} + 1.0004$$

The measured values of the dielectric constants of the vanadium compounds at approximately 25°C . are given in Table IV.

My value for the dielectric constant of VOCl_3 differed from the only previously recorded value³³ by - 0.5. I am unable to explain this variation since the previous work appeared to have been carefully done.

The expected error for the measurements should not be greater than ± 0.008 . The principal sources of error were the lack of reproducibility noted with air in the cell and a variation in the temperature of the cell during measurement and calibration.

TABLE IV

Dielectric constants of the pure vanadium compounds

compound	dielectric constant at 25°C.
vanadium oxytrichloride.....	2.898
vanadium tetrachloride	3.107
ethyl orthovanadate	3.333
n-propyl orthovanadate	2.961
i-propyl orthovanadate	3.299
n-butyl orthovanadate	2.780
i-butyl orthovanadate	2.761
s-butyl orthovanadate	2.969
t-amyl orthovanadate	2.764

PHYSICAL PROPERTIES OF THE SOLUTIONS

Solution Densities

Following a short search of the literature, the magnetically controlled float method of Lamb and Lee³¹ was chosen for measuring densities needed in this work. This method is capable of extreme precision. Lamb and Lee obtained density values with a probable error of less than one unit in the seventh decimal place. Its chief advantage is that it allows density measurements under almost anhydrous conditions, a necessary precaution for working with these very hygroscopic vanadium compounds.

The method is quite simple. A glass float containing a small magnet or piece of soft iron is completely immersed in the liquid whose density is to be measured. The liquid and float are contained in a glass cell and the entire assembly is immersed in a thermostat. A force downwards on the float is exerted by a magnetic field created by a solenoid located under the cell. For a given position of the float, in this case the cell bottom, this force is assumed to be proportional to the current in the solenoid. An upwards force is experienced by the float proportional to its volume and to the difference in density between the float and its surroundings. When the two forces are in balance

$$k_i = gV_f(d-d_f)$$

where: k = force per unit current exerted on the float by the solenoid

i = current in the solenoid

g = acceleration of gravity

V_f = volume of float

d_f = density of float

d = density of the liquid

rearranging this equation, we obtain,

$$d = (k/gV_f)i + d_f$$

The density of the liquid is a linear function of the solenoid current.

The most direct method for calibration of the float; that is, the determination of the equilibrium current in solutions of known density, is not practical in this case. The standard liquids must be known accurately to at least the 5th decimal place. While not unreasonable, measurements of this accuracy are time consuming and require much care. For this reason, an alternative method was used for the calibration.

If the mass and density of the float are known, the float may be calibrated by the successive addition of weights of known mass and density in a liquid of known density. The density difference corresponding to a mass M of density d_M is given by the following relationship:

$$\Delta d = \frac{M}{V_f} \left(1 - \frac{d_{\text{soln.}}}{d_M} \right)$$

By observing the equilibrium currents corresponding to a series

of added weights, the float constant ($\Delta d/i$) can be obtained from the slope of a plot of the calculated density differences against the observed equilibrium currents. This calibration was conducted before and after each series of measurements. The volume of the float was obtained from its weight and density. The latter was found by adjusting a liquid to the exact density of the float and determining the density of the liquid with a pycnometer.

The apparatus was constructed as shown in Figure 15. Water in the thermostat was heated by an infrared lamp and continuously circulated by an external pump. According to the manufacturer, the Kinetic Instrument Co., control to 0.002°C is possible.

The watertight aluminum box containing the solenoid was held in place by twin brass tubes bolted to a wooden support, which was notched to rest firmly on the top of the bath. The pyrex cell had approximately 100 ml capacity. The solenoid was a 170 ohm, square wound coil from the junk box. The pyrex cell was held in position by a metal ring on the watertight box and a notch in the support.

The floats were constructed of pyrex tubing and test tubes. They contained cylindrical magnets similar to those in magnetic stirrer bars. Crude adjustment of the float density was made by adding mercury to the float; the final adjustment, after sealing, by varying the amount of glass on the handling ring. (The handling rings served to allow removal and manipulation of the floats and provided a place for the platinum

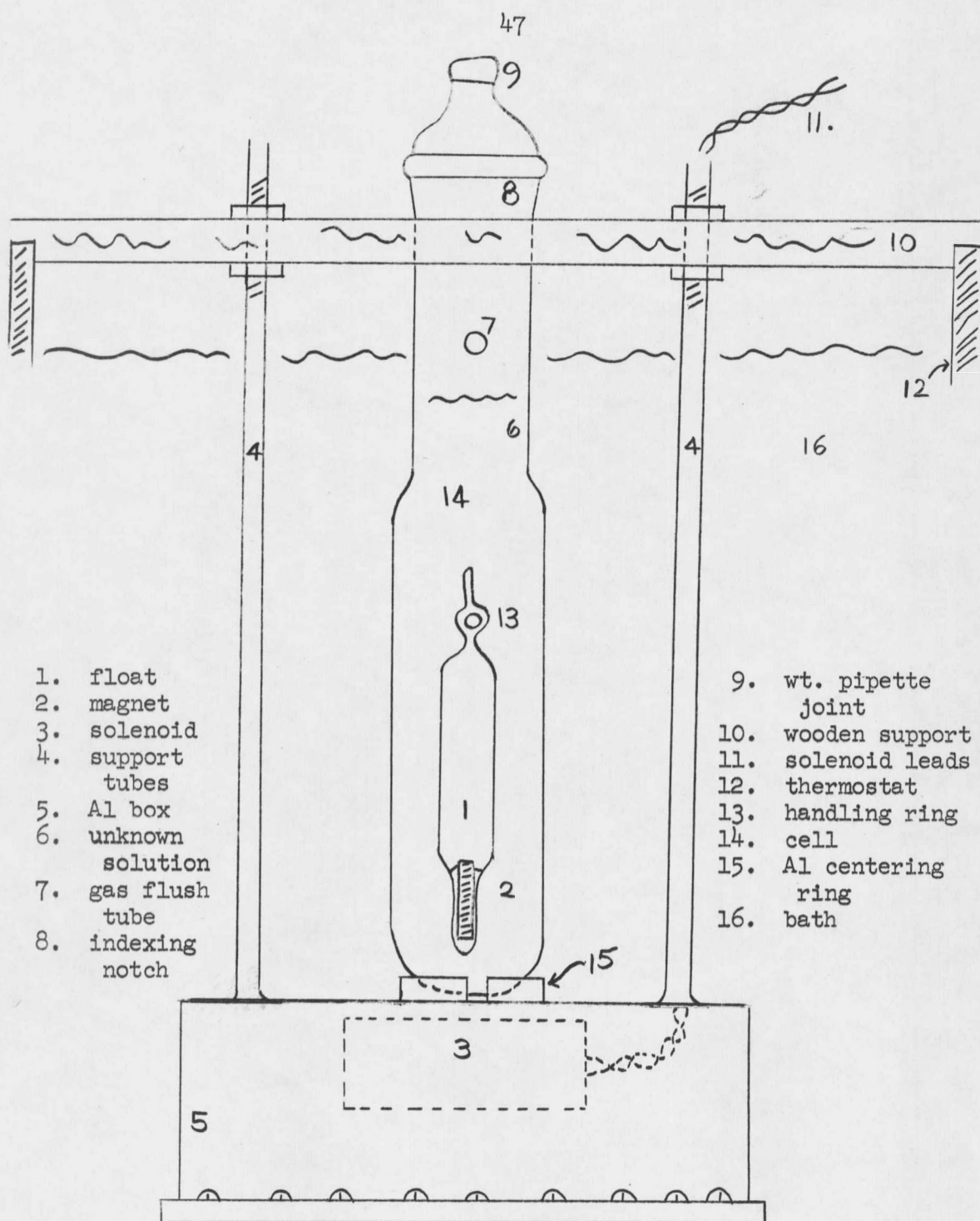


Figure 15 ----- Solution Density Apparatus

wire weights to be placed during the calibration). The float was adjusted so that it just floated in the pure solvent at the proper temperature.

The current supply for the solenoid consisted of four "D" flashlight cells connected in series with a 5,000 ohm helical potentiometer. The circuit is shown in Figure 16.

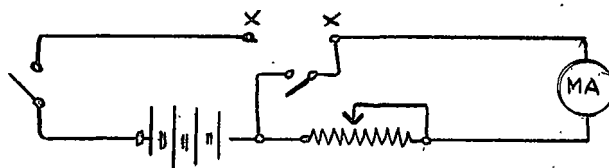


Figure 16

A pushbutton switch was incorporated in the circuit which made it possible to short out the milliammeter and the potentiometer when a momentary current large enough to pull the float into position was desired. The milliammeter was a multirange instrument made by the Sensitive Research Instrument Corp. The accuracy claimed was 1/2% of full scale. The 0-10 ma. range was used.

The apparatus was operated as follows. Solvent was weighed into the cell, the float added, and the assembly placed in the thermostat. When temperature equilibrium was reached, the solenoid current was increased to its maximum. The pushbutton was depressed until the float was in position at the bottom of the cell. The current was decreased rapidly until the float just broke free, and the current was noted. This gave the approximate equilibrium current. Next the current was increased slightly and the float pulled into position at the cell bottom

by depressing the pushbutton. The pushbutton was released and the current slowly decreased in a regular manner. The current at which the float just broke free of the bottom was the equilibrium current. The milliammeter reading was recorded and the process was repeated to insure reproducibility.

A weighed addition of the solute was made to the solvent in the cell. Mixing was accomplished by removing the cell from its position and swirling it by hand in the thermostat bath. A spinning motion of the float was caused and mixing could be completed in a few seconds. The cell was returned to position and the measurement of equilibrium current repeated. This was done for each addition of solute until sufficient points were obtained.

Results of the float calibrations

Benzene Float -- 24.7°C.

float constants =	5.660	$\times 10^{-4}$	$\Delta d/ma$
	5.678	"	"
	5.726	"	"
	5.674	"	"
	5.697	"	"

$$\text{average} = 5.687 \times 10^{-4} \Delta d/ma$$

$$\text{float equation} \dots\dots d = 0.87200 + 5.687 \times 10^{-4} i(ma)$$

Carbon Tetrachloride Float -- 25°C.

float constants =	2.411	$\times 10^{-3}$	$\Delta d/ma$
	2.465	"	"
	2.493	"	"

$$\text{average} = 2.458 \quad " \quad "$$

$$\text{float equation} \dots\dots d = 1.5858 + 2.458 \times 10^{-3} i(ma)$$

The measured currents were converted to densities using the float equations and the densities obtained were plotted against the mole fraction of solute. These graphs will be found in the Appendix.

Under the assumption that the density is a linear function of the concentration, density equations were obtained from the measured data with the aid of the MSC IBM-650 computer. They are listed in Table V.

The equations are valid for a concentration range of 0-20 millimole fraction and are in the unrounded form used in the calculations. Changes in density should be accurate to ± 0.00003 while absolute densities should not be better than ± 0.0001 .

TABLE V

Solution density equations

<u>Compound</u>	<u>Equations</u>
vanadium oxytrichloride	$d = 1.5858 + 0.2263 N_2$
vanadium tetrachloride	$d = 1.5858 + 0.2456 N_2$
ethyl orthovanadate	$d = 0.87354 + 0.5019 N_2$
n-propyl orthovanadate	$d = 0.87360 + 0.4517 N_2$
iso-propyl orthovanadate	$d = 0.87355 + 0.40736 N_2$
n-butyl orthovanadate	$d = 0.87355 + 0.4412 N_2$
iso-butyl orthovanadate	$d = 0.87355 + 0.4027 N_2$
sec-butyl orthovanadate	$d = 0.87358 + 0.3990 N_2$
tert-butyl orthovanadate	$d = 0.87346 + 0.3574 N_2$
tert-amyl orthovanadate	$d = 0.87354 + 0.3905 N_2$

Solution Refractive Indices

Solution measurements of refractive index were made only on VCl_4 and VOCl_3 . The solvent was CCl_4 .

The refractive indices of the solutions were measured with a modified Bausch and Lomb dipping refractometer. The proper prism was cemented into the mouth of a 125 ml round-bottomed flask to which an additional 12 mm. tube had been sealed. Dry CCl_4 was weighed into the flask, which was then attached to the dipping refractometer and the entire assembly was immersed in a thermostat to the level of the upper part of the prism. Weighed additions of the halides were made to the contents of the flask through the 12 mm. tube, the refractive index being measured after each addition. A 60 watt incandescent bulb outside the thermostat supplied the illumination.

During use, the prism is inaccessible inside the flask. Calibration of the prism was therefore not performed.

Assuming that the square of the refractive index is a linear function of the concentration, the appropriate equations were developed by the method of least squares. This data was needed for the calculation of the molar refraction of the halides with the extrapolation equation corresponding to the Hedestrand equation for total polarization. This is a standard procedure for the calculation of polarizations. Further, the experimental curves obtained for n_D^2 vs. mole frac. were essentially linear.

The results of the least squares calculations are as follows:

$$\begin{array}{ll} \text{VOCl}_3 \text{ at } 25^\circ\text{C.} & n_D^2 (\text{solution}) = 2.12786* + 0.524 N_2 \\ \text{VCl}_4 \text{ at } 25^\circ\text{C.} & n_D^2 (\text{solution}) = 2.12786* + 0.6420 N_2 \end{array}$$

where N_2 is the mole fraction of the halide.

Solution dielectric constants

The apparatus used for the measurement of the dielectric constants of solutions is the same as was used for the dielectric constant of the pure liquids except that a jacketed reservoir of about 100 ml. capacity was added to the cell. Water from a thermostat was circulated through both jackets for temperature control.

The solutes were weighed into the combined cell-reservoir from a small weight pipette whose lower joint matched the 14/20 joint at the top of the reservoir.

The cell was calibrated with benzene and cyclohexane. Benzene and cyclohexane were dried by refluxing over metallic sodium and fractionally frozen several times. The values of the dielectric constants of pure benzene and pure cyclohexane were obtained from the American Institute of Physics Handbook².

	<u>20°C.</u>	<u>25°C.</u>	<u>26°C.</u>
Benzene	2.2836	2.2736	2.2716
Cyclohexane	2.0250	2.0172	2.0157

* ---- calculated from values in the literature for the index refraction of CCl_4 .

The following values for the cell constant were obtained using benzene as a standard: 24.73 μmfd , 24.72 μmfd , and 24.72 μmfd . With cyclohexane as a standard the following values for the cell constant were obtained: 24.76 μmfd , 24.75 μmfd , 24.74 μmfd , and 24.74 μmfd . Therefore, for the calculations of the dielectric constants of solutions of the vanadium orthoesters in benzene the cell constant 24.74 μmfd was used.

The solution dielectric constant measurements of VCl_4 and VOCl_3 were performed several months earlier than the corresponding measurements of the esters. For the halides, the cell was calibrated with hexane and the cell constant was 23.62 μmfd . The difference between the cell constant used for the halide solutions and that used for the orthoester solutions may represent damage caused by cleaning, impurity of the standard liquids or inconsistency between the standard dielectric constants of hexane and benzene. The error caused by this difference, if any, is negligible compared to other errors present.

The experimental procedure was as follows. After the apparatus had become stabilized, the readings of the precision condenser were taken with the air-filled cell in place and with it removed. Approximately one mole of solvent was weighed into the cell. The reading of the precision condenser was taken at resonance with the cell in place and with the cell removed. A weighed addition of the vanadium compound was made using the weight pipette. The cell was shaken to mix the added solute. The readings of the precision condenser were taken again

with the cell in place and removed. The next addition of the compound was made and the capacitance readings at resonance were taken as above, until a sufficient number of points were obtained.

Calculations of the dielectric constant were obtained with the following expression:

$$\epsilon/\epsilon_v = \Delta C / \text{cell const.} + 1.0004$$

where ΔC is the difference between the precision capacitance readings with the airfilled cell and the liquid filled cell.

Dielectric constants were plotted against the mole fraction and graphs are given in the Appendix.

Assuming that the dielectric constant of a solution is a linear function of the concentration, the appropriate equations were developed by least squares methods from the data obtained from these measurements. The IBM-650 computer was utilized. The results of these calculations are given in Table VI.

TABLE VI

Solution dielectric constant equations

<u>Compound</u>	<u>Equations</u>
vanadium oxytrichloride	$\epsilon_{12} = 2.2283 + 0.6601 N_2$
vanadium tetrachloride	$\epsilon_{12} = 2.2275 + 0.8782 N_2$
ethyl orthovanadate	$\epsilon_{12} = 2.2731 + 2.4662 N_2$
n-propyl orthovanadate	$\epsilon_{12} = 2.2748 + 2.2256 N_2$
iso-propyl orthovanadate	$\epsilon_{12} = 2.2709 + 2.4267 N_2$
n-butyl orthovanadate	$\epsilon_{12} = 2.2729 + 2.0641 N_2$
iso-butyl orthovanadate	$\epsilon_{12} = 2.2703 + 1.9568 N_2$
sec-butyl orthovanadate	$\epsilon_{12} = 2.2716 + 1.6978 N_2$
tert-butyl orthovanadate	$\epsilon_{12} = 2.2705 + 2.108 N_2^*$
tert-amyl orthovanadate	$\epsilon_{12} = 2.2731 + 1.924 N_2$

*This value is likely to show error as considerable curvature was apparent.

Molecular weight measurements

Molecular weights of the esters were determined by a cryoscopic method using benzene as solvent. The freezing temperatures of solvent and solutions were measured by the resistance of a thermistor, which was placed in one arm of a Wheatstone bridge. The unbalanced voltage of the bridge was fed to a recorder, for convenience in the necessary extrapolation of the thermistor resistance to its value at the start of freezing. Agitation was accomplished with a solenoid actuated stirrer.

A block diagram of the apparatus is given as Figure 17.

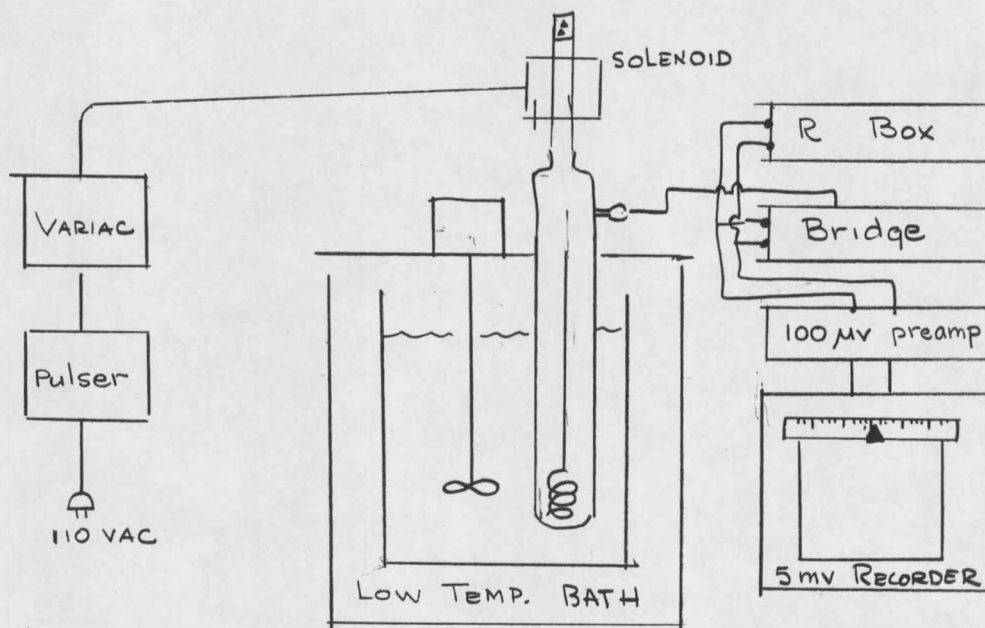


Figure 17

The recorder was a "Brown" 5 mv. potentiometer, Model #153 x 12-V-II-III-156, with a four second pen speed. The preamplifier was a "Brown" chopper amplifier with a 50 X amplification factor.

It was found necessary to use shielded leads for all connections between the bridge and the amplifier because of the radiation of the solenoid magnetic field. A Leeds and Northrup 4 decade resistance box was connected in parallel with the bridge output to allow variation in the sensitivity of the bridge since both the recorder and preamplifier ranges were fixed. The preamplifier raised the signal level from the bridge to a level permitting high sensitivity and matched the bridge impedance to the recorder.

The bridge was a Leeds and Northrup student Wheatstone bridge. It was powered with a single 1.5 v. telephone type dry cell. The thermistor was a 2000 ohm (at room temperature) glass enclosed bead. The manufacturer's specifications give this thermistor a resistance ratio, $R(0^{\circ})/R(50^{\circ})$, of 7.3 and a dissipation constant of one milliwatt/deg.

The stirrer was driven by an AC solenoid, Guardian Electric #4, with 24 oz. lift at intermittent duty. This solenoid was modified by removing the armature and drilling through the metal frame so that a 12 mm. dia. tube would just slip through. The voltage applied to the solenoid was varied with a Variac, normally set at 50-60 volts. The pulser was a unit designed by Dr. L. O. Binder of this department for use in controlling the reflux ratio of fractionating columns⁴⁸. It was

modified by lowering the capacitance of the storage capacitors to produce a faster pulsing rate. The rate was 60-80 pulses per minute. This represented the maximum pulse rate possible with the components used, however, an increased rate would have been desirable.

The controlled, low temperature bath was constructed at this institution and consisted of a two stage refrigerator, with the second stage evaporating coil soldered to a 12" x 12" x 12" galvanized metal tank. The refrigerator was capable of a temperature of $-60^{\circ}\text{C}.$, controlled to within $\pm 1^{\circ}\text{C}.$ The tank was insulated with about 3" of packed glass wool. The lid was a 4" slab of foamed polystyrene lined with masonite and contained holes for the insertion of the cell, bath controlling thermistor and a motor driven stirrer. The bath was a solution of ethanol or ethylene glycol. The temperature of the bath was regulated with a Fenwald Thermistor controller which operated the compressor power relays.

The cell is shown in Figure 18.

The solution level was maintained just over the thermistor well. This corresponded to a volume of approximately 70 ml. Solute was added through a weight pipette placed in a standard taper joint at the top of the cell. This joint was tilted so that the drops of the solute would fall near the axis of the cell. The large solution volume limited determinations in this apparatus to rather dilute solutions unless large amounts of solute were available.

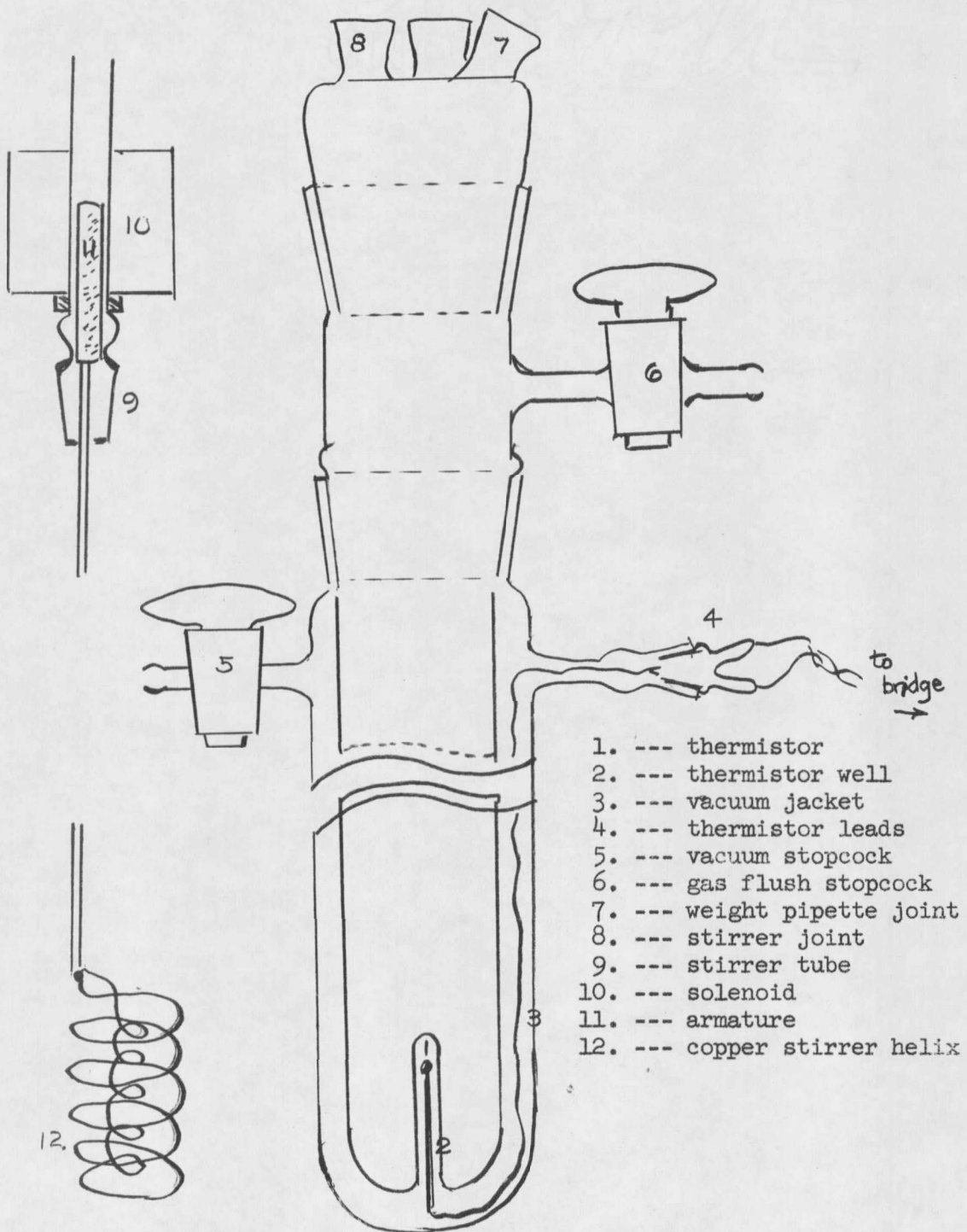


Figure 18

Freezing point apparatus

The thermistor leads were twisted together inside the vacuum jacket and they were led out through the side tube. A 10/30 pyrex joint fitted with two Housekeeper seals allowed connections to be made to the bridge. Shielded wire was not used for this section of the leads but would have been desirable.

The stirrer assembly consisted of a double helix of copper wire attached to a 1/4" diameter brass rod. The upper section of this rod was threaded so that it could be screwed into a 12 mm. pyrex tube which was sealed to a 14/35 male joint. A large diameter ring cut from suitable rubber tubing was placed over the outside of the pyrex tube to position the solenoid. A shock absorber, made from several short sections of thin walled rubber tubing, was placed in the lower part of the tube to absorb the impact of the falling armature.

A small amount of silicone high vacuum grease was placed in the thermistor well to establish thermal contact.

The resistance of thermistors can be represented by the following approximate equation.

$$\ln (R/R_0) = \beta (1/T - 1/T_0) = \beta \Delta T / TT_0$$

Since only the temperature difference is required, this equation can be arranged to

$$\Delta T = (TT_0/\beta) \ln R/R_0$$

where β = a constant characteristic of the thermistor

T_0 = f.p. of solvent

T = f.p. of solution

R_0 = resistance of thermistor at the f. p. of solvent

R = resistance of thermistor at the f. p. of solution.

Now, where ΔT is small compared to T , an approximation can be written as

$$\Delta T = (T_0^2) \ln R/R_0$$

Calibration of the thermistor was accomplished by measuring the freezing points of benzene and water. The benzene used was dried and fractionated before use. A small amount was further purified by several fractional crystallizations, but the freezing temperature did not appear to change. All samples of benzene gave horizontal freezing curves. A few hundred ml. of cyclohexane was put through a similar purification procedure but its freezing point did not agree with the reported values. Since flat freezing curves were not obtained, it was not used for calibration.

The following is a summary of the results:

	<u>f. p.</u>	<u>ave. R</u>
Benzene	5.533°C.	4502.3 $\pm$ 1.0 $\sim$
Water	0.00°C.	5702.7 $\pm$ 1.0 $\sim$

Rearranging the basic resistance formula

$$\beta = TT_0/\Delta T \ln R/R_0$$

Calculated from the average values above, the thermistor used has a β of 3256 using the freezing points of benzene and water.

The following formula was used for the calculation of the temperature depression: $\Delta T = 23.85 \ln R/R_0$.

TABLE VII

Molecular weights of alkyl orthovanadates

mole frac. $\times 10^3$	molecular wt.	Theo. mol. wt.
<u>ethyl orthovanadate</u>		
9.27	188	202.1
14.94	194	"
<u>n-propyl orthovanadate</u>		
6.11	225	244.2
12.64	267	"
<u>i-propyl orthovanadate</u>		
2.97	218	244.2
10.32	226	"
16.25	225	"
<u>n-butyl orthovanadate</u>		
5.16	312	286.3
8.54	263	"
13.71	276	"
<u>s-butyl orthovanadate</u>		
2.81	269	286.3
6.51	286	"
10.42	273	"
<u>i-butyl orthovanadate</u>		
4.06	285	286.3
7.20	263	"
9.25	276	"
<u>t-butyl orthovanate</u>		
1.17	262	286.3
2.75	248	"
<u>t-amyl orthovanadate</u>		
1.164	280	328
4.596	289	"
8.119	298	"
11.069	302	"

CALCULATIONS

DISCUSSION

The total polarization (P_T) of a substance can be expressed by a function of the molecular weight, density and dielectric constant of the substance. This relationship, the Clausius-Mosotti equation is as follows:

$$P_T = \frac{(\epsilon - 1) M}{(\epsilon + 2) d}$$

where

ϵ = dielectric constant

M = molecular weight

d = density

The total polarization is the sum of several polarizations, the electronic polarization (P_E), the atomic polarization (P_A) and the orientation polarization (P_O). The electronic polarization is a result of the distortion of the electrons in atoms caused by the electric field. The atomic polarization is caused by distortion of the position of the atoms with respect to one another in the field. It is usually a small term in comparison to the electronic polarization. The orientation polarization is the result of the alignment of the permanent dipoles of the molecules with the applied field. It is a function of the size of the permanent dipole and the temperature of the measurement. The orientation polarization is of interest as part of a method of determining the size of the permanent dipoles. The size of the dipole, which

is the product of the charge and the distance of separation, is the electric moment.

Electric moments are generally expressed in debye units which are 10^{-18} e.s.u.-cm. The Debye equation expresses the relation between the electric moment, the temperature and the orientation polarization

$$P_O = \frac{4\pi N\mu^2}{9kT}$$

where μ = electric moment

N = Avagadro's number

k = Boltzman's constant

T = Temperature ($^{\circ}$ K)

Solving this equation for the electric moment and using the proper numerical values in the equations, one obtains:

$$\mu = 0.01281 \sqrt{P_O T} \quad (\text{Debyes})$$

Since the orientation is the only polarization term that is temperature dependent, it can be obtained by measuring the total polarization over a suitable (large) range of temperatures or by determining the total polarization, the electronic polarization and the atomic polarization and subtracting the latter two quantities from the first.

$$P_O = P_T - P_E - P_A$$

The evaluation of these polarization terms for the substances studied will be discussed in the subsequent sections of this thesis.

TOTAL POLARIZATION

The total polarization of a solution is the sum of that due to the solute and that due to the solvent.

$$(P_T)_{12} = N_1 P_1 + N_2 P_2$$

N = mole fraction
1 = solvent
2 = solute

Thus measurements of dielectric constant and density of solutions of known concentration should enable one to calculate the polarizations of both solute and solvent. Actually, this equation is not used directly because when the concentration becomes small, the solution polarization and the solvent contribution become nearly equal and the relative error may become quite large.

To overcome this difficulty, several equations have been developed taking advantage of the common linear relationship between the dielectric constant and concentration of solutions. The Halverstadt and Kumler equation²⁸ takes the specific volume as a linear function of the concentration. The Hedestrand equation²⁷ considers the density as a linear function of concentration.

Both equations yield identical results and for this work the Hedestrand equation was used. This equation is as follows:

$$P_{2\infty} = A (M_2 - B\beta d_1) + C\alpha\epsilon_1$$

where ϵ_1 = dielectric constant of solvent

d_1 = density of the solvent

M_2 = Molecular weight of solute

$P_{2\infty}$ = Total Polarization of the solute
at infinite dilution

and α and β are obtained from the following equations:

$$\epsilon_{12} = \epsilon_1 (1 + \alpha c_2)$$

$$d_{12} = d_1 (1 + \beta c_2)$$

and

$$A = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{1}{d_1} \quad B = \frac{M_1}{d_1} \quad C = \frac{3M_1}{(\epsilon_1 + 2)^2 d_1}$$

A, B, and C are constants for any one solvent.

As illustrated in the previous sections, the necessary slopes were obtained by least squares calculations performed on the sets of density-mole fraction and dielectric constant-mole fraction data with the aid of the IBM-650 computer.

The vanadium compounds are considered to be monomers on the strength of the molecular weight measurements.

Using monomeric molecular weight, and the density-mole fraction and dielectric constant-mole fraction equations, the total polarization of each compound was calculated using the Hedestrand equation.

TABLE VIII

Slopes, constants and results of the calculations of Total Polarization

compound	ϵ_1 ***	d_1 ***	A	B	C	α	β	M_2	P_T
VOCl_3^*	2.2283	1.5858**	0.1832	97.01	16.278	0.2963	0.1427	173.32	38.48
VCl_4^*	2.2275	1.5858**	0.1831	97.01	16.28	0.39425	0.1549	192.78	45.23
Et_3VO_4	2.2731	0.87354	0.3411	89.415	14.691	1.085	0.5746	202.13	89.86
Pr_3VO_4	2.2748	0.87360	0.3413	89.409	14.678	0.9784	0.5171	244.21	102.24
Pr_3^iVO_4	2.2709	0.87356	0.3406	89.413	14.705	1.0864	0.4663	244.21	107.06
$\text{Bu}_3^{\text{iv}}\text{VO}_4$	2.2729	0.87355	0.3410	89.414	14.692	0.9081	0.5051	286.29	114.50
Bu_3^iVO_4	2.2703	0.87355	0.3405	89.414	14.710	0.8619	0.4610	286.29	114.01
Bu_3^sVO_4	2.2716	0.87358	0.3408	89.411	14.700	0.7474	0.4567	286.29	110.36
Bu_3^tVO_4	2.2705	0.87346	0.3406	89.424	14.710	0.9285	0.4092	286.29	117.63
Am_3^tVO_4	2.2731	0.87354	0.3411	89.415	14.691	0.8464	0.4470	328.36	128.35

* ----- The solvent was CCl_4
 ** ----- The literature values were used

*** ----- The values (except as noted)
 are the intercepts of the
 ϵ vs. N_2 and d vs. N_2 plots

ATOMIC POLARIZATION

This portion of the total polarization is the result of the changes in position of the atomic nuclei in the molecule with respect to one another. Changes in dipole moment of the molecule occur when the interatomic distances change as a result of bending or twisting or oscillation of the polar groups with respect to each other. While atomic polarizations are not additive, estimates can be made by comparison with similar molecules for which estimates of atomic polarization are available.

The principal requirement for a sizeable atomic polarization are polar bonds and suitable motions (usually bending) involving these bonds.

The low atomic polarizations of the saturated hydrocarbons are a result of the low moments of the C-H and C-C bonds. The low atomic polarization of tetranitromethane, on the other hand, is very likely due to the mutual steric hindrance of the nitro groups; except for this, tetranitromethane would be expected to have a large atomic polarization. Quite large atomic polarizations are usually observed for molecules in which sufficiently free bending motions occur and where these motions involve highly polar bonds. Examples are given by Smyth⁵³. For example, thorium acetylacetonate has an atomic polarization of 77 cc.

Direct measurements of the atomic polarization are difficult and inaccurate. It has been suggested that P_A can be estimated as the difference between the polarization of a substance in its solid form

and the electronic polarization in the liquid form. This assumes that no orientation polarization is possible in the solid form. When substances are reliably nonpolar, as in tetrahedrally or octahedrally symmetrical compounds, the atomic polarization can be considered to be the difference between the total polarization and the electronic polarization extrapolated to infinite wavelength. Another method is to plot total polarization against $1/T$, the intercept at $1/T = 0$ being taken as the total of the electronic and atomic polarization. Subtracting the electronic polarization, determined from molar refraction, will give a value for the atomic polarization.

Equations have been developed for the calculation of the atomic polarization from the force constants of the motions and the bond moments involved. An example is the equation of Coop and Sutton⁴⁹, developed for tetrahedral molecules, AX_4 .

$$P_A = \frac{16\pi N \mu^2}{9V} \quad \begin{array}{l} \mu = \text{bond moment} \\ V = \text{force constant} \end{array}$$

Since the molecular spectra of the vanadium compounds (except $VOCl_3$) have not been examined in detail, no values for these force constants of the vibrations of the polar bonds of the vanadium compounds are available.

In the present work, measurements were made at one temperature only, which precludes the extrapolation method. The substances are partially polar, ruling out another method. No measurements of the

polarization of the solids were made which eliminates still another method.

Since the necessary data for a direct calculation of the atomic polarization was neither available nor measured, the atomic polarizations were estimated from the known values of similar or related compounds.

These estimates are available for molecules at least formally similar to both VOCl_3 and VCl_4 ⁵³ and are included as Table IX.

TABLE IX

Atomic polarizations of some halides

CCl_4	2 cc
SiF_4	5.4 cc
TiCl_4	5 cc
GeCl_4	8 cc
COCl_2	2 cc
CF_3Cl	4 cc
SOCl_2	4 cc

The atomic polarization of VCl_4 should be similar to TiCl_4 , since both are tetrahedral and both central atoms are similar. This indicates an atomic polarization of about 5 cc for VCl_4 , which is good agreement with the other measured polarizations (see rest of calculations). For VOCl_3 , the problem is less clear cut but an estimate of from 2 to 5 cc should be reasonable.

The chemical reactivity of VOCl_3 is low for reactions where polar-polar attractions might be expected to be important. For example, VOCl_3 can be refluxed with metallic Na without effect, while similar treatment of CCl_4 with metallic Na can lead to a violent reaction. On the other hand, the rapid hydrolysis of VOCl_3 is likely due to a different (addition-substitution) reaction mechanism. On this account, a low value of 2 cc was taken as reasonable for the atomic polarization.

An estimate of the expected atomic polarization of the esters is more difficult and the possible uncertainty larger than for the halides, since values of the atomic polarization for similar compounds are not available. Considering the atomic polarization of the molecule as an additive function of its parts, total can be obtained by evaluating each part. Molecules of known atomic polarization can be used to estimate the contribution of structures which are part of the total molecule.

The contribution of the C-H bonds to atomic polarization is small but can be estimated since accurate data is available for the hydrocarbons. The principal structures contributing to the atomic polarization should be the bending motion about the oxygens (three of these motions/molecule) the V(OR)_3 deformation and a small contribution from the V-O bond. The C-O-V bending contribution can be estimated from the atomic polarization of ethyl ether and butyl ether, less a small amount for the hydrocarbon bonds in these compounds. This gives 2.8 cc per VO-C. The contribution of the V(OR)_3 deformation is guessed

to be 2 cc. The hydrogen-carbon contribution is 0.1 cc/carbon. A value of 0.5 cc for the V-O bond is used, since this is a stretching motion. Summing these contributions, the following estimates for the atomic polarizations were found and, along with estimates for the halides, are given in Table X.

TABLE X

Estimated Atomic Polarizations

VOCl_3	2 cc	Et_3VO_4	11.5 cc
VCl_4	5 cc	Pr_3VO_4	11.8 cc
Am_3VO_4	12.4 cc	Bu_3VO_4	12.1 cc

It should be remembered that the entire atomic polarization term is only a minor percentage of the electronic polarization. A lack of rigor in the estimates is unlikely to introduce serious error into an electric moment determination. In some papers, the entire atomic polarization term is neglected or a small arbitrary fraction of the electronic polarization on molar refraction was used.⁵⁰

ELECTRONIC POLARIZATION

The electronic polarization of each of the esters was found by computing its molar refraction (R_D) using the measured values of density and index of refraction and then taking 96% of the computed value as the electronic polarization. The 4% correction represents the observed average difference between R_D and P_E ⁵⁰. Molar refractions for the pure liquids were calculated using the following equation based upon the Lorentz-Lorenz equation.

$$R_D = \frac{(n_D^2 - 1) M}{(n_D^2 + 2) d}$$

where

n_D = refractive index for the D line

d = density

M = molecular weight

In the case of $VC l_4$ and $VOCl_3$, R_D was computed from the measurements of the density and index of refraction of solutions of the halides using an equation of the form of the Hedestrand equation. No correction was made to the values of R_D in the case of the halides which were used as the electronic polarizations.

The following is a list of the Molar Refractions and electronic polarizations obtained from them.

TABLE XI

Molar Refractions and Electronic Polarizations

compound	R_D (cc)	P_E (cc)
vanadium oxytrichloride	35.03	35.03
vanadium tetrachloride	39.98	39.98
ethyl orthovanadate	51.98	49.90
n-propyl orthovanadate	66.27	63.62
i-propyl orthovanadate	66.96	64.28
n-butyl orthovanadate	80.06	76.86
i-butyl orthovanadate	80.55	77.33
s-butyl orthovanadate	80.71	77.48
t-butyl orthovanadate	81.06*	77.82
t-amyl orthovanadate	94.66	90.87

* ----- This value was calculated from the table of atomic refractions and from the R_D values of the other esters since it is a solid.

ELECTRIC MOMENT

The electric moments of the vanadium compounds were calculated using the Debye equation

$$\mu = 0.01281 \sqrt{P_O T}$$

$$\text{where } P_O = P_T - P_A - P_E \quad \text{and} \quad P_E = 0.96 R_D$$

Several equations have been developed for the calculation of the electric moment from the physical properties of the pure substance. Onsager's equation³⁹ in a slightly modified form⁵³ is the most popular.

$$\mu = 0.01281 \times 10^{-18} \sqrt{\frac{MT}{d} \frac{(2\epsilon + n_D^2)(\epsilon + 2)}{3\epsilon(n_D^2 + 2)} \left[\frac{(\epsilon - 1)}{(\epsilon + 2)} - \frac{(n_D^2 - 1)}{(n_D^2 + 2)} \right]}$$

where

ϵ = dielectric constant of pure liquid

n_D = index of refraction of pure liquid

d = density of pure liquid

M = Molecular weight of pure liquid

Table XII lists the various polarizations, and the electric moments, calculated from both solution data and the Onsager equation.

TABLE XII

Calculations of the electric moment -- Summary

compound	P _T	R _D	P _E	P _A	P _O	μ_{soln}	μ_{Onsager}
VOCl ₃	38.48	35.03	35.03	2	1.5	0.31 D	0.39 D
VDl ₄	45.23	39.98	39.98	5	0	0 D	not available
Et ₃ VO ₄	89.86	51.98	49.90	11.5	28.46	1.18	1.16
Pr ₃ ⁿ VO ₄	102.24	66.27	63.62	11.8	26.82	1.15	1.11
Pr ₃ ⁱ VO ₄	107.06	66.96	64.28	11.8	30.98	1.23	1.40
Bu ₃ ⁿ VO ₄	114.50	80.06	76.86	12.1	25.54	1.12	1.09
Bu ₃ ⁱ VO ₄	114.01	80.55	77.33	12.1	24.58	1.10	1.10
Bu ₃ ^s VO ₄	110.36	80.71	77.48	12.1	20.78	1.01	1.30
Bu ₃ ^t VO ₄	117.63	81.06	77.82	12.1	27.71	1.16	---
Am ₃ ^t VO ₄	128.35	94.66	90.87	12.4	25.08	1.11	1.22

DISCUSSION

Palmer⁴¹ and Lipscomb and Whittaker³², using electron diffraction methods, have measured the interatomic distances and angles in VOCl_3 and VCl_4 in the vapor phase. VCl_4 is arranged tetrahedrally while VOCl_3 has a slightly distorted tetrahedral arrangement.

Infrared and Raman studies^{13,38} of liquid VOCl_3 indicate the molecule to possess C_{3v} symmetry, corresponding to the structure found by the electron diffraction data. Our cryoscopic molecular weight measurements, taken in CCl_4 solution as a part of this study, do not agree with the infrared and Raman studies. The indicated molecular weight was greater than the value expected for the monomer. However, since solid solutions are known to exist in the VCl_4 - CCl_4 system⁵⁹, our inability to show the absence of a solid solution in the solid phase makes these cryoscopic measurements unreliable. We conclude that the molecule of VOCl_3 is the same in both liquid and vapor phases.

Assuming the bond distances and angles obtained for the vapor phase to hold for the liquid as well, one can construct a table of distances and angles in VCl_4 and VOCl_3 . These values are given in Table XIII. The sums of the singly bonded covalent radii of atoms corresponding to the listed bonds, are included for comparison of interatomic distances. The discrepancies will be discussed later.

TABLE XIII

Interatomic distances and angles

bond or angle	VOCl_3	VCl_4	sum of covalent radii
V-Cl	2.12 Å ^o	2.03 Å ^o	2.21 Å ^o
V-O	1.56 Å ^o	—	1.94 Å ^o
∠ Cl-V-Cl	111°17'	109°28'	—
∠ Cl-V-O	108°12'	—	—

Our electric moment measurements are consistent with a tetrahedral structure for VCl_4 . For this configuration, the V-Cl bond moments cancel one another producing the observed zero electric moment.

One of the objectives of this study was, if possible, the measurement of the individual bond moments of the V-Cl and the V-O bonds. Since VCl_4 was found to be tetrahedral we can make no direct measurement of the V-Cl bond moment. Unfortunately, the bond moment of the V-Cl bond in VOCl_3 as well as the electric moment of the molecule must be known to calculate the V-O bond moment.

While the V-Cl bond moment is not directly available, we can estimate it from the electronegativity differences of the V and Cl atoms. The electronegativities of V and Cl are as follows.

$$X_V = 1.9$$

$$X_{\text{Cl}} = 3.0$$

Assuming covalent character of the bonds, the difference between the electronegativities, (1.1), leads to an estimate of 1.1 debyes for

the V-Cl bond moment. This value should be considered only as an approximation, since estimation of bond moments from electronegativity differences can give incorrect moments, especially if the bonds are highly polar.

In VOCl_3 the V-O bond and the three V-Cl bonds have their moments in opposition. Using the Cl-V-O bond angle of $108^\circ 12'$, the total molecular moment can be expressed as a function of the two moments as follows;

$$\mu_{\text{VOCl}_3} = |\mu_{\text{V-O}} - 0.967 \mu_{\text{V-Cl}}|$$

if the bond moment of the V-Cl bond is 1.1 debye then we find the relation becomes;

$$\mu_{\text{VOCl}_3} = |\mu_{\text{V-O}} - 1.06|$$

Using the measured electric moment of VOCl_3 (0.3 ± 0.3 debye), we can calculate the V-O bond moment.

$$\mu_{\text{V-O}} = 1.4 \pm 0.3 \quad \text{or} \quad 0.8 \pm 0.3 \text{ debyes.}$$

Two ranges of values are possible since either the V-O bond moment of the resultant of the three bond moments could be larger. The lower range seems unlikely however and will be disregarded.

Instead of using the electronegativity difference between V and Cl to determine the V-Cl bond moment, we can estimate it by correcting the observed moment for a similar bond by an amount equal to the electronegativity difference between the Vanadium and the other element. We shall pick the P-Cl bond because of the close relationship between phosphorus and vanadium and because of the similarity of many of their

The moment of the P-Cl bond is 0.81 debyes¹⁵ assuming PCl_3 to have an electric moment of 1.1 debyes. Using a PCl_3 electric moment of 0.9 debyes¹⁵, it is 0.66 debyes. Since the electronegativity difference between V and P is 0.2, the V-Cl bond can be estimated as 0.88 or 1.01 debyes. Using these values in the equation obtained above and assuming that the V-O bond is larger than the resultant of the 3 V-Cl bonds the V-O bond moment is found to be 1.3 or 1.2 debyes, depending upon which value for the P-Cl moment is used.

The properties of VOCl_3 correspond to a compound with low bond moments. The low boiling point, low freezing point, total miscibility with non-polar solvents, regular Trouton's constant and low dielectric constant all indicate a substance with small bond moments.

A large V-O bond moment, compensated by a large V-Cl bond moment could produce the observed electric moment of VOCl_3 . However, this would require a relatively large charge on the central vanadium atom. Such a distribution of charges rarely occurs.

POCl_3 , the phosphorus analog of VOCl_3 , has an electric moment of 2.4 debyes⁵¹. The electric moment of VOCl_3 is 0.3 debyes. The moment of the P-O bond has been estimated as 2.7 debyes¹⁴ and 3.3 debyes¹⁵ with the last value being best established. Our estimate for the V-O bond moment is approximately 1.4 ± 0.3 debyes.

Providing the V-O moment is considerably smaller than the P-O moment, as is indicated, one should be able to observe the effect of

this difference on the dielectric constants of closely related vanadium and phosphorus compounds. As an example, consider the dielectric constants of the n-butyl esters of orthovanadic and orthophosphoric acids.

$$\epsilon/\epsilon_v (\text{Bu}_3^{\text{n}}\text{PO}_4) = 8.05 \quad \epsilon/\epsilon_v (\text{Bu}_3^{\text{n}}\text{VO}_4) = 2.79$$

While one cannot be certain that the V-Cl bond moment is not unexpectedly large, which would raise our estimates of the V-O bond moment, we feel the present evidence indicates our estimate of a 1.4 ± 0.3 debyes to be quite reasonable.

An explanation for the low moment of the V-O bond can be found in the assumption of pi bonding between the V and the O atoms. A similar hypothesis has been suggested by Whittaker and Lipscomb³² to account for the short V-O and V-Cl distances in VOCl_3 and VCl_4 .

The ground state of vanadium is $3d^3 4s^2$. The observed tetrahedral configurations in VOCl_3 and VCl_4 can be explained by assuming d^3s hybrid bonding. This would either require the promotion of one of the 4s electrons to the 4p orbitals, making it possible for the formation of a pi bond with one of the 2p orbitals of the oxygen atom, or alternatively, require the donation of two electrons to the oxygen atom with the consequent formation of a coordinate covalent bond.

An "ideal" coordinate covalent bond would have unit electronic charge of opposite sign on each of the partners in the bond. This would provide an electric moment of 4.8 debye per Angstrom of separa-

tion. Using the measured distance for the V-O bond ($1.56\text{\AA}$), we can calculate the "ideal" moment of 7.50 debye for the coordinate covalent V-O bond. On the other hand, an "ideal" pi bond would have no electric bond moment since the electrons would be shared equally between the atoms. These ideal situations do not appear to exist. Bonds classified as coordinate covalent have considerably smaller moments than the "ideal" value. Smyth⁴⁹ has suggested a range of 35-65% of the theoretical value as typical of the coordinate covalent bond.

Pi bonds between dissimilar atoms could be expected to have a moment, though not a large one, due to asymmetry of the pi bond.

Promotion of an s electron to a p orbital as a preliminary to pi bond formation is not new or novel. Something of the sort must occur during the formation of ethylene to permit the carbon to form the necessary trigonal sp^2 hybrid orbitals.

In vanadium atoms, this process should not be unlikely since the energy values of the orbitals are similar. The 3d and the 4s orbitals are almost identical and the 4p orbitals are only slightly higher.

There is evidence that bonding involving the 4p orbitals of vanadium does occur. Jones²⁷ has shown that the chelates of the VO^{++} ion are consistent with a tetragonal pyramidal structure using either d^2sp^2 or d^3p^3 hybridization. Octahedral bonding of vanadium compounds is known^{14*}.

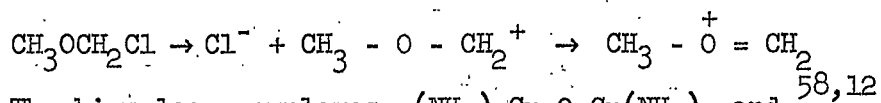
* -- the existence of $V(H_2O)_6^{+++}$, like the similar complex ions of the transition metal group, is known.

Using the estimate of 1.4 debye for the V-O bond moment, one finds that this corresponds to 19% of the theoretical maximum value for the coordinate covalent bond, a value well under Smyth's 35-65% estimate. It would seem then, that pi bonding in VOCl_3 is possible and that our low value for the V-O bond can be explained on this basis.

As can be seen from Table XIII, the bond distances in VCl_4 and VOCl_3 are shorter than the sums of the corresponding covalent radii. As mentioned, Lipscomb and Whittaker³² have discussed this problem and have concluded that there is multiple bonding in both VCl_4 and VOCl_3 . The short V-Cl distances in both the halides are explained as due to partial double bond character in the V-Cl bond. They suggest that the very short V-O distance is the result of partial triple bond character. This additional partial multiple bonding character was surmised to come from the donation of unused electron pairs on the Cl or O atoms to vacant orbitals in the vanadium atom.

Basolo and Pearson, in a recent book³, support the conclusion that pi bonding in which the ligand donates the electron pair is an important process and suggests the following examples as proof.

(a) The high solvolytic activity of alpha-halo ethers can be accounted for on the basis of stabilization of an ionic form by donor pi bonding.



(b) The binuclear complexes $(\text{NH}_3)_5\text{Cr}-\text{O}-\text{Cr}(\text{NH}_3)_5$ and ^{58,12}

$\text{Cl}_5\text{Ru}-\text{O}-\text{RuCl}_5$ both show magnetic properties indicating 4 less unpaired electrons than would be indicated by the simple structures shown here. This can be explained by the formation of pi bonds between the O atom and the Ru or Cr atoms. X-ray measurements of the ruthenium compound show a bond shortening and that the molecule is linear, both corroborating a pi bonding hypothesis.

To summarize, I feel that in addition to a good case for the existence of a low V-O bond moment, a reasonable explanation, i.e., pi bonding in VOCl_3 (and probably in $\text{VO}(\text{OR})_3$), has been developed.

No work has been done of the structure of the esters of orthovanadic acid. Molecular weight measurements* in benzene solution indicate that these esters are monomeric. There is some indication, to be discussed later, that the pure liquids may contain traces of polymeric forms. The electric moments measured for the esters should correspond to the monomeric values.

Table XIV is a comparison of some of the electric moments for the alkyl orthovanadates* and values collected from the literature by Ketelaar²⁸ for the corresponding alkyl orthophosphates.

* --- part of this work

TABLE XIV

Electric moments of the alkyl orthovanadates and orthophosphates

R	$\mu_{R_3PO_4}$	$\mu_{R_3VO_4}$
Ethyl	3.07	1.18
n-propyl	3.09	1.15
i-propyl	2.85	1.23
n-butyl	3.05	1.12

The molecules $VOCl_3$ and $POCl_3$ are similar, both physically and chemically and it seems reasonable to expect similarities for the corresponding alkyl esters.

If one constructs models of the orthophosphate and the orthovanadate esters, using tetrahedral angles, one finds that there will be some restriction of positions of the alkoxy groups. Drawings given below show the two extreme positions of the alkoxy groups.

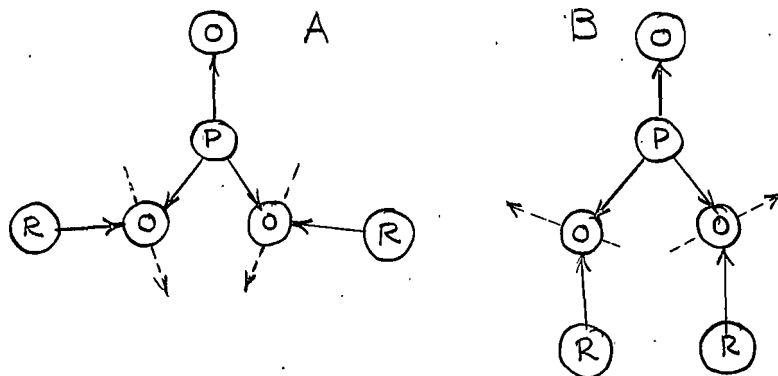


Figure 19

Alternate configurations for the orthovanadates and orthophosphates

Mutual interference between the alkoxy groups is the greatest in configuration B and least in configuration A. Note that the resulting bond moment vector for the POR or VOR group, indicated by the dotted arrow, opposes the V-O or P-O bond moment in A and, in B, aids it only slightly. The bulkier the alkoxy group, the more the configurations corresponding to position A will be favored, resulting in a lower observed moment for the molecule.

Estok¹⁵ points out that this lowering is observed in the electric moment of triphenyl orthovanadate (2.79 debyes) as compared to the alkyl orthophosphates (approx. 3.0 debyes).

In order to discuss steric hindrance to the rotation of the alkoxy groups in the esters, calculations of the expected moments for the esters, assuming free rotation, were made. A general formula for this calculation was developed by Eyring¹⁶. Applying this formula to the case of the esters and assuming tetrahedral bonding angles, the following general relationship can be obtained.

$$u^2 = 3m_1^2 + 3m_2^2 + m_3^2 - 6\cos\theta (m_2^2 + m_2m_3 + m_1m_3) + 6\cos^2\theta (2m_1m_2 + m_1m_3) - 6\cos^3\theta m_1^2$$

where:

θ = the supplement of the tetrahedral angle ($70^\circ 32'$)

m_1 = R-O bond moment

m_2 = V,P -O (alkoxy) bond moment

m_3 = V,P -O bond moment

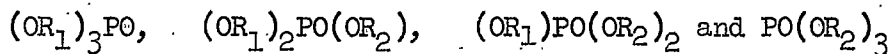
μ = "average" moment of the molecule

Assuming the following estimates for the bond moments found in

the esters of orthophosphoric acid, $m_1 = 1.14$ debye, $m_2 = 1.2$ debye and $m_3 = 3.3$ debyes, the calculated moment, assuming free rotation, was found to be 3.10 debyes. This agrees with the observed values for the simple alkyl orthophosphates. See Table XIV.

For the alkyl orthovanadates, assuming $m_1 = 1.14$, $m_2 = 1.4$ debyes and $m_3 = 1.4$ debyes, the calculated moment for the esters, assuming free rotation, was 1.93 debyes. This is considerably larger than the observed values, which are in the vicinity of 1.1 debyes.

A recent study of the orthophosphate esters was reported by Gersman, Ketelaar and Hartog²⁸. They obtained electric moments for several series of esters of the following types.



where R_1 and R_2 were groups with differing group moments.

Considering the resultant of the POR bond moments to be a single vector, and assuming that the angle between these vectors and the P-O bond vector to be constant for all members of the series and for differing R groups included in the series, they were able to calculate the angle between the POR vector and the PO vector. This was approximately 90° .

Assuming tetrahedral angles for the phosphorus atom, the assumption that the angle between the P-O and POR moment vectors is a constant appears incorrect. The restricted rotation, noted in the models,

should force the RO groups into the "A" configurations, see Figure 19, in which the angle between the vectors should be considerably larger than 90° for groups of similar moment. Among the series investigated were the mixed ethyl phenyl orthophosphates. The angle found $87^\circ 30'$, which would not be expected since the phenoxy and ethoxy group moments should be similar.

A convenient model that will satisfy the 90° vector angle requirement is as follows. Assume that the RO-P-OR bond angles have widened to 120° while the O-P-OR angles have closed to 90° . This would place the three RO-P bonds in a common plane with the P-O bond normal to it. Assuming free rotation, all the POR moment vectors would be directed along the corresponding P-OR bond axis and the 90° vector angle would be found irregardless of the nature of the attached groups.

However, the theoretical electric moment calculated for such a molecule, assuming the bond moments used in the previous calculation and free rotation, is 3.79 debyes which is considerably larger than the observed values for the alkyl orthophosphates (3.1 debyes). This reduction would seem to indicate considerable restriction of rotation which may not be compatible with a 90° vector angle. It appears, therefore, that until supporting evidence concerning the structure of the orthophosphates appears, this model should not be regarded seriously.

A comparison of the observed and calculated electric moments of the alkyl orthovanadates and orthophosphates indicates a contradiction.

Both moments agree in the case of the phosphorus compounds. They do not agree in the case of the vanadium compounds. This indicates a lack of restriction of rotation of the alkoxy groups only in the phosphorus compounds, which seems unusual since the radius of the vanadium atom is 0.1 Angstrom larger than the phosphorus atom. Being larger one would expect that there would be a smaller barrier to restriction in the orthovanadates.

However, there appears to be extensive restriction of rotation in the orthovanadates. There is no combination of V-O or V-OR bond moments that will produce the observed moments and yet permit free rotation about the V-OR axes. Free rotation of the OR groups, alone, should produce a moment of 1.7 debyes.

There is no present evidence to indicate that the alkyl orthovanadates are other than regular monomers. Cryoscopic measurements taken in benzene, at the same concentrations used in the electric moment determinations, indicate this. A preliminary electric moment measurement of ethyl orthovanadate taken in heptane yielded a value of 1.06 debyes. This value is sufficiently close to the value of 1.18 debyes found in benzene solution to eliminate a possible benzene-orthovanadate complex as the cause for a low moment.

On the other hand, there is no evidence that the orthophosphates are other than simple monomers. If the orthophosphates are similar to the orthovanadates, the restricted rotation of the alkoxy groups ob-

served in those compounds should occur in the orthophosphates. Since restricted rotation should lower the observed moment, our previous calculated free-rotation moment would be low.

Changes in three of the variables used in the calculation of the free rotation moment will cause an increase in the theoretical moment of the molecule. These are 1) an increase in the PO bond moment, 2) a decrease in the P-OR bond moment and 3) a decrease in the O-P-OR bond angle. The present value of the bond moment for the P-O bond seems well established. Any sizeable increase would not be consistent with the electric moments of other phosphorus compounds. The value for the P-OR bond moment apparently originated in a paper by Smyth⁵². The value, 1.2 debyes, was obtained by the subtraction of the P-H bond moment from the O-H bond moment. This method was justified by the agreement of the P-X bond moments calculated in this way with the observed values. While this method may be proper in this case, it cannot be used for other bonds. We may be justified in regarding it with some slight suspicion.

It seems quite possible then that an increased free-rotation value for the moments of the alkyl orthophosphates can be justified by a decrease in the P-OR bond moment or the P-O-OR bond angle. This would indicate some restriction of rotation in the alkyl orthophosphates.

We can summarize the last few pages by noting that the paper of Ketelaar, Gersman and Hartog requires further explanation and the apparent restriction of rotation that occurs in the orthovanadates and

not in the orthophosphates indicates the need for further study of the structures of both these types of esters.

Of the compounds covered in this work, only the molecular spectra of VOCl_3 has been previously examined. The Raman spectra was studied by Eichoff and Weigel¹³ and both the Raman and infrared by Miller³⁸. Their conclusions were identical - both assigned the molecule a symmetry of C_{3v} . The assignments of the observed frequencies are given in Table XV.

TABLE XV

Assignment of the observed Raman and IR frequencies of VOCl_3

symmetric vibrations	degenerate vibrations
V-O stretch 1035 cm^{-1}	V-Cl stretch 504 cm^{-1}
O-V- Cl_3 "pulsation" 408 cm^{-1}	O-V-Cl deformation ... 249 cm^{-1}
VCl_3 deformation 165 cm^{-1}	O-V- Cl_3 rocking 129 cm^{-1}

These vibrations are both Raman and Infrared active. The Raman line at 408 cm^{-1} was intense enough to be visible.

With our present instrument, only the V-O stretching frequency is available for study.

Examination of the infrared absorption spectra (see figures 12-14) of the alkyl orthovanadates in the region near 1035 cm^{-1} shows only one absorption peak with consistent frequency and common to all the esters. This is a peak of medium to weak strength near 1010 cm^{-1} . It is con-

siderably obscured by the C-O stretching frequencies of the alkoxy groups. This appears to be the V-O stretching frequency.

This tentative assignment should be checked by preparing and examining some of the compounds reported in the literature that should contain a V-O bond. Examples are the tertiary silyl vanadates⁴⁰ or the compounds, $\text{VO}(\text{NO}_3)_3$ ⁴¹ or $\text{VO}(\text{ClO}_4)_3$ ⁴⁷. The preparation of a suitable compound not containing the V-O group such as $(\text{RO})_3\text{V}$ ₃ should help prove the assignment.

The absorption spectra of the partial hydrolysis product of n-butyl orthovanadate was obtained. This curve showed a strong peak at 1010 cm^{-1} and a small C-H peak. The presence of the V-O groups in this compound is indicated. The molecular weight and composition of these partial hydrolysis products was determined by Prandl and Hess⁴². Both correspond to the formula $\text{R}_3\text{V}_3\text{O}_9$. A recent paper dealing with the structure of the metaphosphate esters presents a suitable structure for these hydrolysis compounds (9).

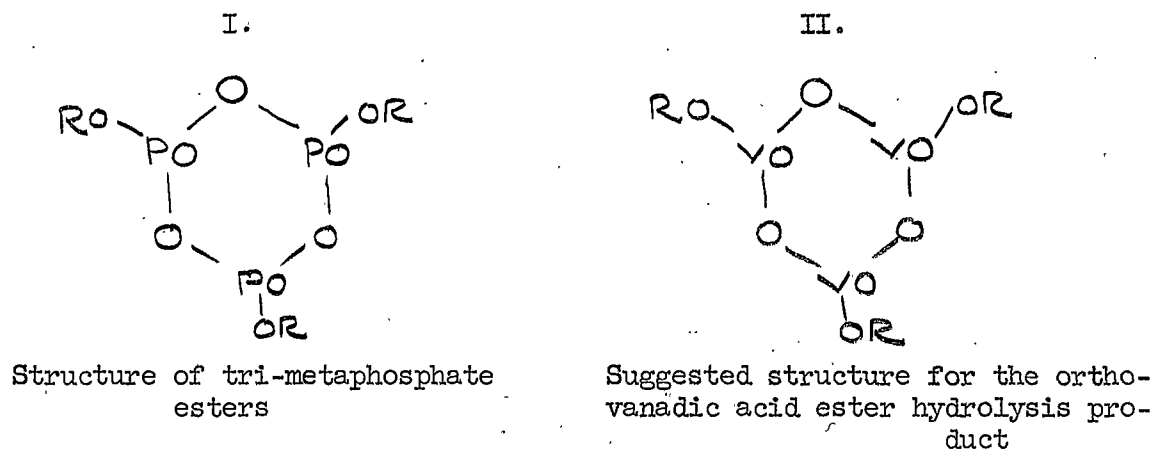


Figure 20

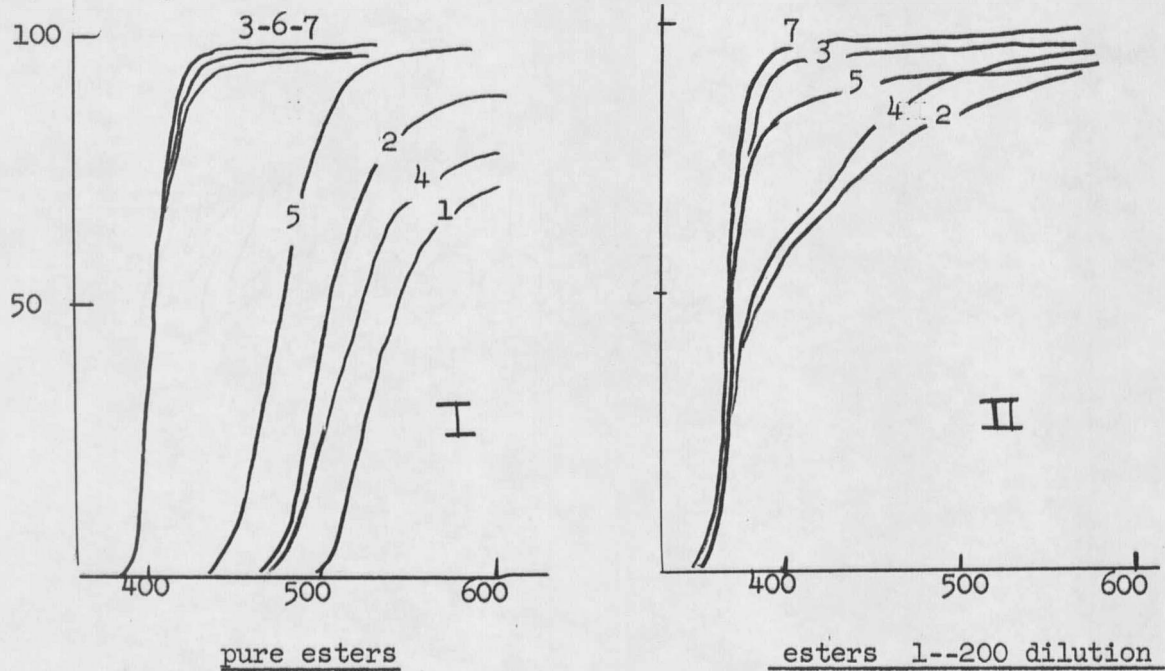
The presence of a color in some of the esters and its absence in others requires an explanation. The isopropyl, secondary butyl, tertiary amyl orthovanadates are colorless. The isobutyl is pale yellow in color and the normal butyl esters are lemon colored. The ethyl ester is a yellow-orange color. These colors are reflected in the visible spectra illustrated in Figure 21, part I. There is intense absorption in the ultraviolet with the cut-off frequencies shifting further into the visible as the esters become more colored. All the colorless esters cutoff sharply at wavelengths just below 400 mμ.

Part II of Figure 21 illustrates the effect of dilution. The spectra represent a 200X dilution over the esters in part I. The solvent was n-heptane. The strong absorptions exhibited by the pure colored esters in the 400 to 500 mμ range are quite weak and all the esters have a cutoff at about 350 mμ.

Two possible explanations for these observed phenomenon seem possible. Of these, the first is the more likely.

First, the liquid esters are principally monomeric but color in the colored esters is due to a small fraction of a polymeric form of the esters. The esters which are highly branched, a deterrent of polymerization, are colorless. The straight chain esters where steric hindrance is the least troublesome are the most highly colored. Isobutyl orthovanadate in which the carbon chain branches in the beta position is only palely yellow.

Upon dilution of the esters the equilibrium existing between the monomer and polymer would shift towards the absorption in the 400-450 m μ region.



- | | | | |
|------------|-------------|-------------|------------|
| 1) Ethyl | 2) n-propyl | 3) i-propyl | 4) n-butyl |
| 5) i-butyl | 6) s-butyl | 7) t-amyl | |

Visible absorption spectra of the alkyl orthovanadic acid esters

Figure 21

A shift to the red upon polymerization should occur. The corresponding yellow $\rightarrow$ orange shift for the chromate - dichromate system is well known, as are the orange polymeric vanadates formed upon the addition of acid to aqueous solution of metavanadates.

Finally, the observed solution values of the electric moments of the colorless esters are lower than the values obtained with the Onsager equation. The colored esters however (see Table XII) have lower values for their Onsager moments. Normally, the Onsager values are larger. For isobutyl vanadate, both values are the same.

Since the Onsager value for the electric moment is based on the properties of the pure liquids, it could be expected that the Onsager moment would reflect a change in structure of the pure liquids from the state in the solution. Since one would expect that the polymeric form of the esters would have a higher symmetry and lower electric moments, the observed variations support this hypothesis.

Second, the alternative explanation is that the esters are monomeric and that the color is due to the presence of difficultly separable hydrolysis products. However, multiple vacuum distillations have not caused a change in the color of the esters. Additions of moisture, as observed in handling and in the slow decomposition noted, do cause a deepening of color, but this is lost upon redistillation.

It may be possible to settle the question of the existence of polymers of the esters by broad band n.m.r. measurements using the V^{51}

nucleii. Walchii and Morgan⁵⁷ have found that VOCl_3 gives a V^{51} resonance separated by about 3 gauss from the position of vanadates and other vanadium compounds tested. It seems that since a polymer might be expected to present the vanadium atom with an environment different from that of the monomer and similar to the vanadates so that two peaks might be observed in the n.m.r. V^{51} spectra of the colored esters. If exchange were rapid, a single peak whose position shifted towards the VOCl_3 position upon dilution only for the colored esters would indicate the presence of polymers in the esters.

All the esters show intense absorption in the ultraviolet. The wavelength of the maximum has not been located yet since the esters appear either to hydrolyze with the traces of moisture encountered upon dilution and handling or show photodecomposition from the ultraviolet radiation. Better drying procedures for the solvents and improved apparatus and handling technique should permit the investigation of this absorption peak.

Using the values listed below for the atomic refraction and using molar refractions obtained from the densities and indices of refractions of the pure liquids, the group refraction for the VO group can be calculated. Table XVI lists the atomic refractions used for the calculations.
46,11

TABLE XVI

Atoms	Atomic refractions
-C	2.592 cc
-C-	2.418 cc
H-	1.100 cc
-O- (ester)	1.64 cc
O= (ketonic)	2.21 cc
Cl-	5.97 cc

Table XVII presents the resulting values for the VO group refraction and the compounds from which they were determined.

TABLE XVII

ethyl vanadate	15.53 cc
n-propyl vanadate	15.97 cc
i-propyl vanadate	16.13 cc
n-butyl vanadate	15.90 cc
i-butyl vanadate	15.87 cc
s-butyl vanadate	16.03 cc
t-amyl vanadate	15.61 cc
Average =	<u>15.86 cc</u>

Using this average value, the molar refraction for t-butyl vanadate was calculated to be 81.06 cc. and this value was used for the electric moment calculations.

It would be of interest to compare the VO group refraction just obtained with the value obtained from VOCl_3 . Using the value of 5.97 cc as the atomic refraction of the Cl atom and the pure liquid molar refraction value for VOCl_3 of 33.98 cc, a value 16.10 cc is calculated as the VO group refraction. This differs from the average obtained from the esters by 0.24 cc and is within the range found in the esters indicating that the VO groups in the ester and in VOCl_3 are similar.

It has been frequently observed that the atomic refraction of an oxygen atom that is pi bonded (ketones for example) is "exalted" above its normal value. "Exaltation" of the oxygen in the V-O bond would be indicative of pi bonding.

According to a recent paper²¹ dealing with the bond refractions in phosphorus compounds, the P-O bond refraction is smaller than expected. Examples of other coordinate covalent bonds with low or negative bond refractions are provided leading to the conclusion that a negative or unexpectedly low bond refraction is indicative of a coordinate covalent bond.

The refraction data we have obtained is insufficient to test for the absence or presence of pi bonding using these hypotheses. More accurate index of refraction data on vanadium compounds, may permit

the application of these tests and help indicate the type of VO bond occurring in VOCl_3 .

The preceding discussion can be summarized with the following statements.

- (1) The V-O bond moment has been estimated as 0.8 or 1.4 debyes using the measured value of 0.3 debyes for the electric moment of VOCl_3 , the angles found in the electron diffraction study and a bond moment for the V-Cl bond estimated from the electronegativity difference and chemical activity.
- (2) Two independent values for the P-Cl bond moment, obtained from measurements of the PCl_3 electric moment, were corrected by the electronegativity difference between P and V to obtain a value for the V-Cl bond moment. These V-Cl bond moments were then used, with the electric moment of VOCl_3 to obtain estimates of 1.3 or 1.2 debyes for the V-O bond moment.
- (3) The physical properties of VOCl_3 indicate that the compound is composed of bonds of low moment.
- (4) The estimates of the V-O bond moment as approximately 1.4 debyes can be explained by considering the tetrahedral symmetry of these compounds to be due to d^3s hybrid bonding and the low electric moments observed in VOCl_3 and the alkyl orthovanadates to be due to pi bonding between the V and O atoms.

(5) Assuming free rotation of the alkoxy groups, values for the electric moments of the alkyl orthovanadates and orthophosphates were calculated. The observed electric moments of the orthovanadates are much lower than the calculated values indicating considerable restriction of rotation. In view of the probable similarity between $\text{VO}(\text{OR})_3$ and $\text{PO}(\text{OR})_3$, some restriction of rotation in the orthophosphates seems possible, although its existence was not shown.

(6) The infrared spectra of the alkyl orthovanadates have been examined and a peak of weak to medium intensity near 1010 cm^{-1} that appears to be the V-O stretching frequency has been found.

(7) By analogy to a phosphorus compound, a cyclic structure for the partial hydrolysis product of the orthovanadates is suggested.

(8) The V-O group refraction was found to be 15.86 cc. The refraction data was insufficient to show either the existence or absence of pi bonding in VOCl_3 .

(9) It has been suggested that the color found in several of the esters is due to the presence of a fraction of the ester in a polymeric form.

SUGGESTIONS FOR FUTURE WORK

- (1) The V^{51} n.m.r. spectra of $VOCl_3$, VCl_4 and the alkyl orthovanadates should be investigated. Polymers may show their presence by producing additional peaks or by broad peaks which shift or change width upon dilution. As large a temperature range as possible should be used to check the possibility that rapid exchange of the V atoms is hiding some peaks or that some polymers are only stable at lower temperatures.
- (2) Electric moments of several of the alkyl orthovanadates and orthophosphates should be measured over a large temperature range to determine the absence or presence of restricted rotation in the phosphorus and vanadium compounds.
- (3) The X-ray diffraction patterns of liquid $VOCl_3$ and of the alkyl orthovanadates should be investigated. Although this method would require considerable labor and extensive use of the IBM 650, it should be possible to check the structure of $VOCl_3$ in the liquid form. It is possible that the presence of polymeric forms of the esters could be detected without the necessity of a complete analysis.
- (4) The Viscosity and vapor pressure of the esters over a range of temperatures should be determined. These are useful for the characterization of these compounds and, providing the heats of vaporization for a series of the esters can be measured, the presence of polymeric forms may be indicated by larger heats of vaporization, or activation energy of viscous flow expected for a polymeric ester.

(5) The esters of orthovanadic acid should be examined for stability to light, and if suitable wave lengths of light can be used, the Raman spectra of the esters should be obtained. This information will help in the definite assignment of the infrared absorption frequencies.

(6) In order to verify the tentative assignment of the peak near 1010 cm^{-1} as the V-O stretching frequency, several more compounds which contain the VO group, such as $\text{VO}(\text{ClO}_4)_3$, $\text{VO}(\text{NO}_3)_3$, $(\text{R}_3\text{SiO})_3\text{VO}$, VOBr_3 and VOF_3 should be prepared as well as several related compounds which do not contain the VO group such as VSCL_3 , or the alkyl thioesters, $(\text{RO})_3\text{PS}$. A study of the infrared spectra of these compounds should permit the definite assignment of the V-O stretch frequency and very likely, the V-OR and the V-S stretching frequencies as well. This study should be carried into the KBr or CsBr regions when the apparatus becomes available.

(7) The V-O bond moments estimated in this study should be confirmed. Providing a series of mixed halides, such as VOCl_3 , VOCl_2Br , VOClBr_2 and VOBr_3 can be prepared and isolated, their electric moments should be measured. This information should allow solution for the V-Cl, V-Br, V-O bond moments as well as the O-V-X angles. If the Cl-Br series are not stable, the Cl-F series or the chloro ester series could be utilized. Similarly, the mixed vanadium (IV) halogen-esters recently reported by Bradley⁵ may provide a series suitable for the measurement of the V-X and V-OR bond moments.

(8) The conductivity of ethanol-ethyl orthovanadate solutions reported by Prandl and Hess⁴² may indicate the presence of ionic forms such as $\text{VO}(\text{OR})_4^-$, since both components are poor conductors. The presence of such forms may be shown by conductivity measurements or by the isolation and analysis of the silver or barium salts.

(9) The crystal structure of solid VOCl_3 should be investigated by X-ray diffraction techniques. Cl n.m.r. studies have indicated that the solid contains two non-equivalent chlorine atoms. This may be similar to recently reported NbOCl_3 ⁴⁴ solid structure.

(10) The freezing points of the esters should be measured accurately, with special attention to the existence of supercooling.

(11) The phase diagram of the $\text{VOCl}_3\text{-CCl}_4$ system should be obtained using cooling curve techniques. Both items (10) and (11) can be conveniently done with a 100 μv recorder using thermocouples as temperature sensing elements.

(12) The kinetics of the hydrolysis of the alkyl orthovanadates should be studied. A spectrophotometric technique using the absorption peak in the near uv region should be suitable.

(13) The kinetics of the apparently autocatalytic decomposition of the orthovanadates at elevated temperature should be investigated. The pressure of the gas evolved should provide a method for the measurement of the extent of the pyrolysis.

(14) The $\text{V}(\text{OR})_4$ esters have not yet been isolated. This may be

possible by reduction with potassium metal as has been done for the $\text{Ti}(\text{OR})_3$ esters. When isolated, these compounds will be helpful in the assigning of the characteristic V-OR frequency.

(15) Finally, the corresponding chromium esters have become important as oxidation intermediates. The use of the vanadium esters for this purpose should be investigated.

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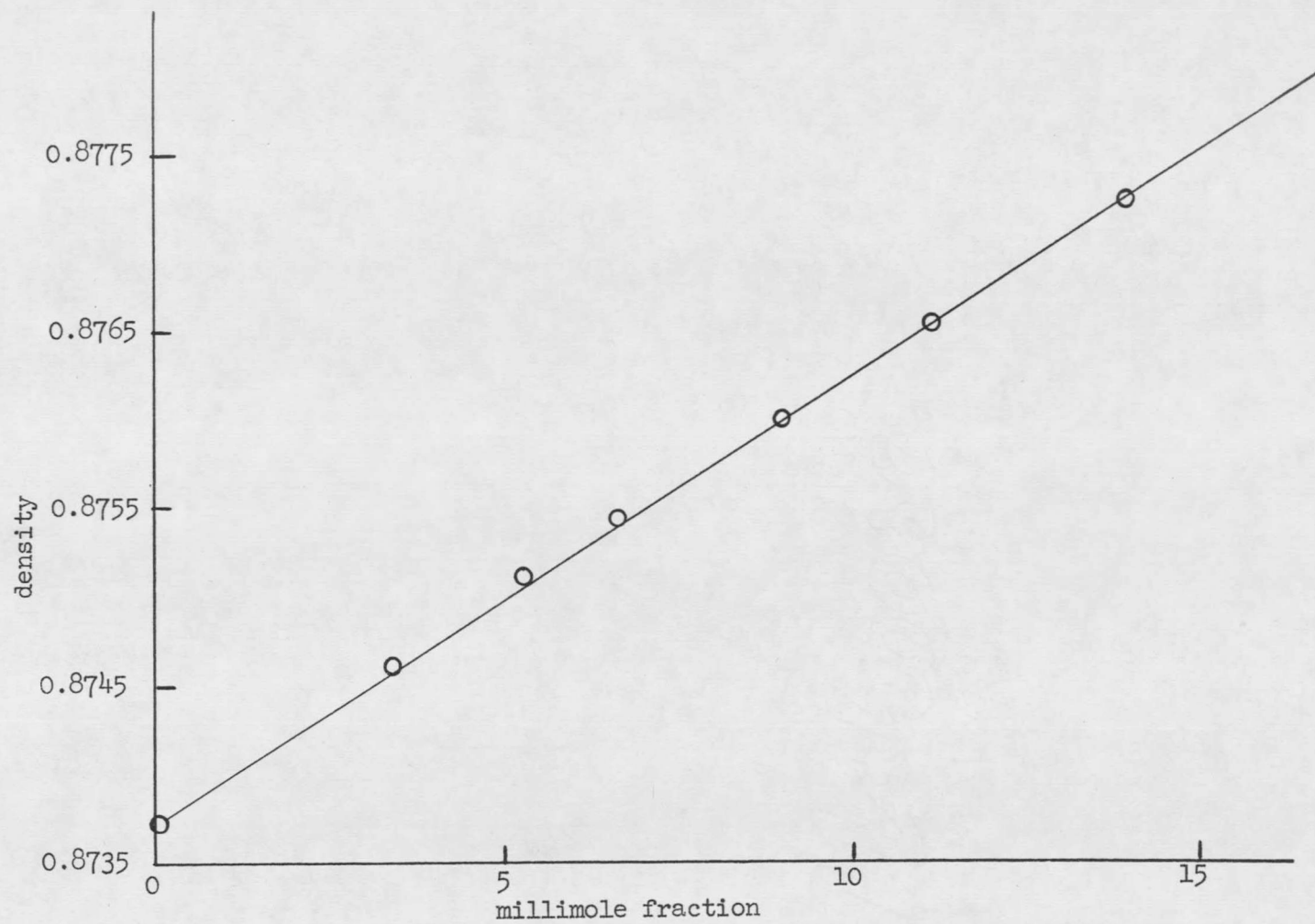
Dr. Bruce Murray in running the n.m.r. spectra and interpreting it.

Dr. Norman Birkholz who prepared the VOCl_3 and to

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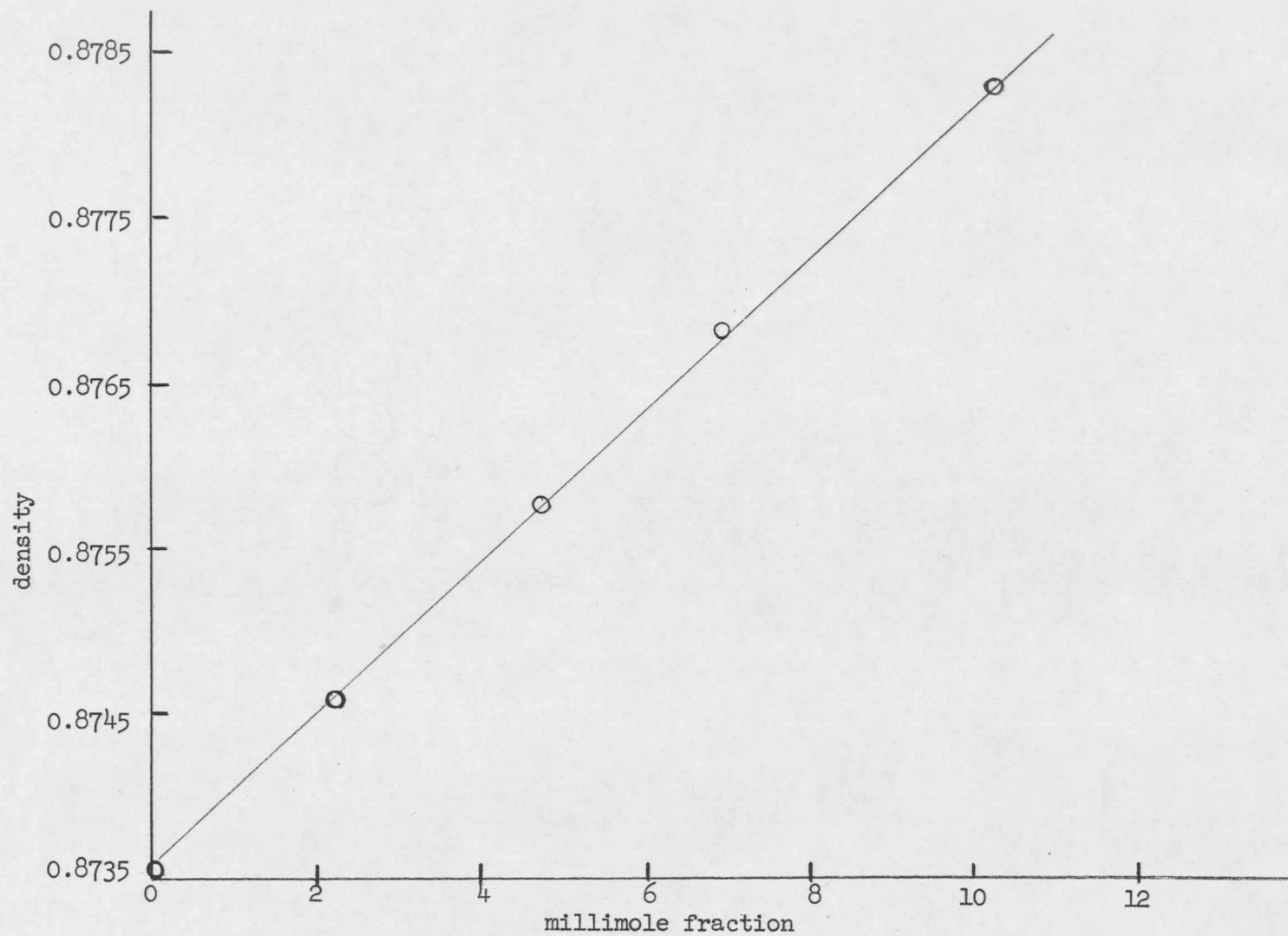
Finally, I wish to express my grateful appreciation for the financial assistance made possible by the Office of Ordnance Research, U. S. Army.

APPENDIX

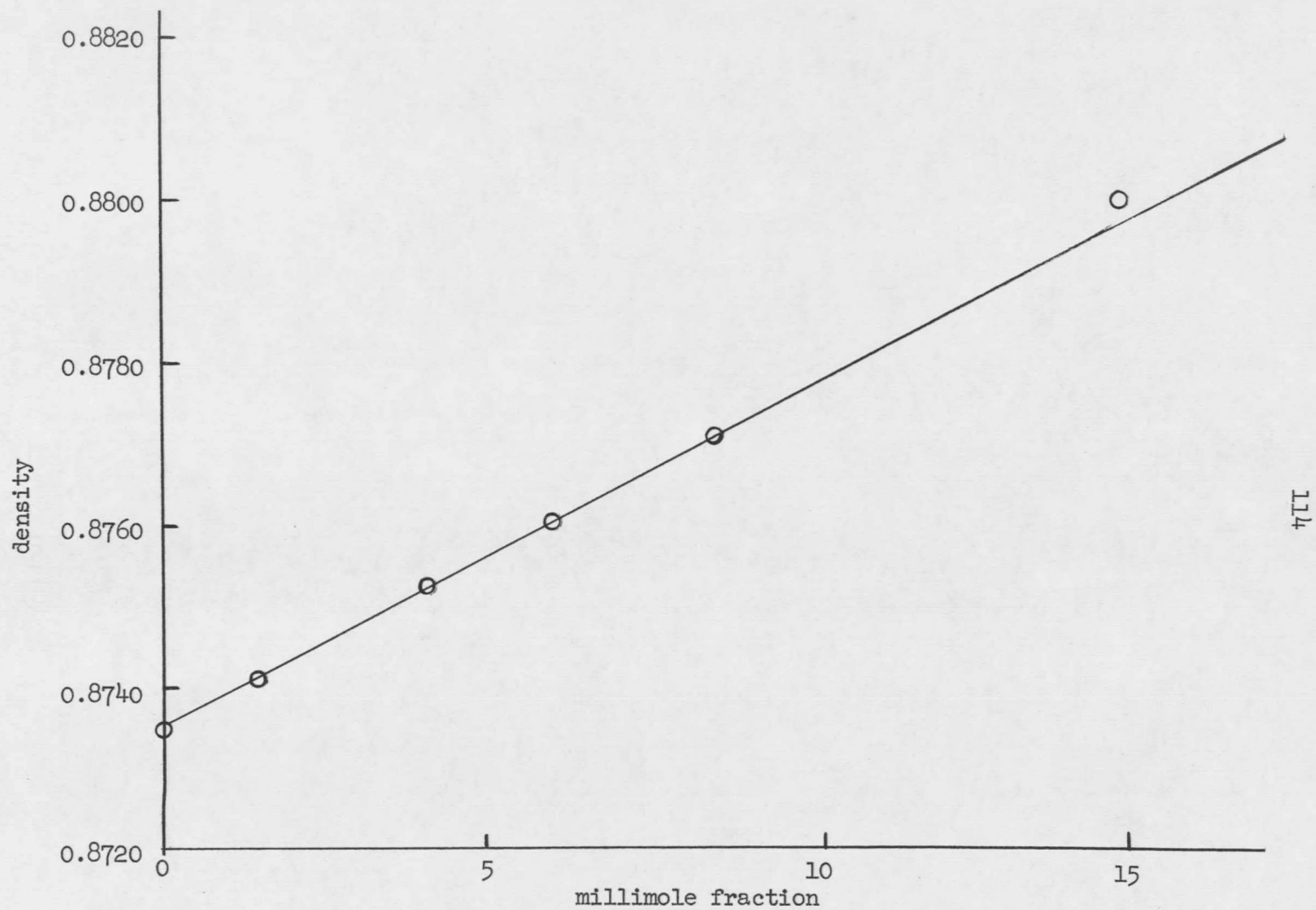


density vs. millimole fraction

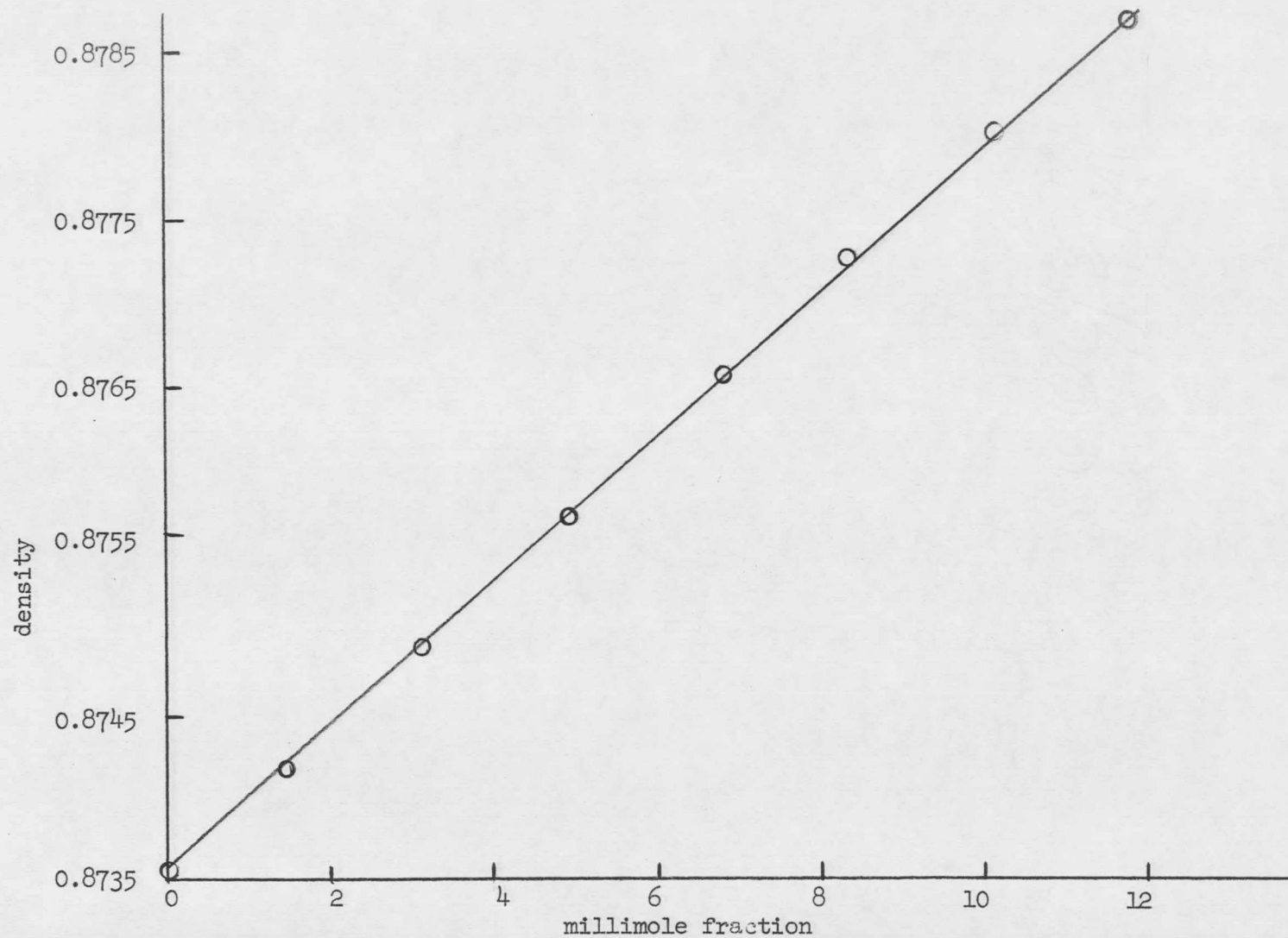
ethyl orthovanadate



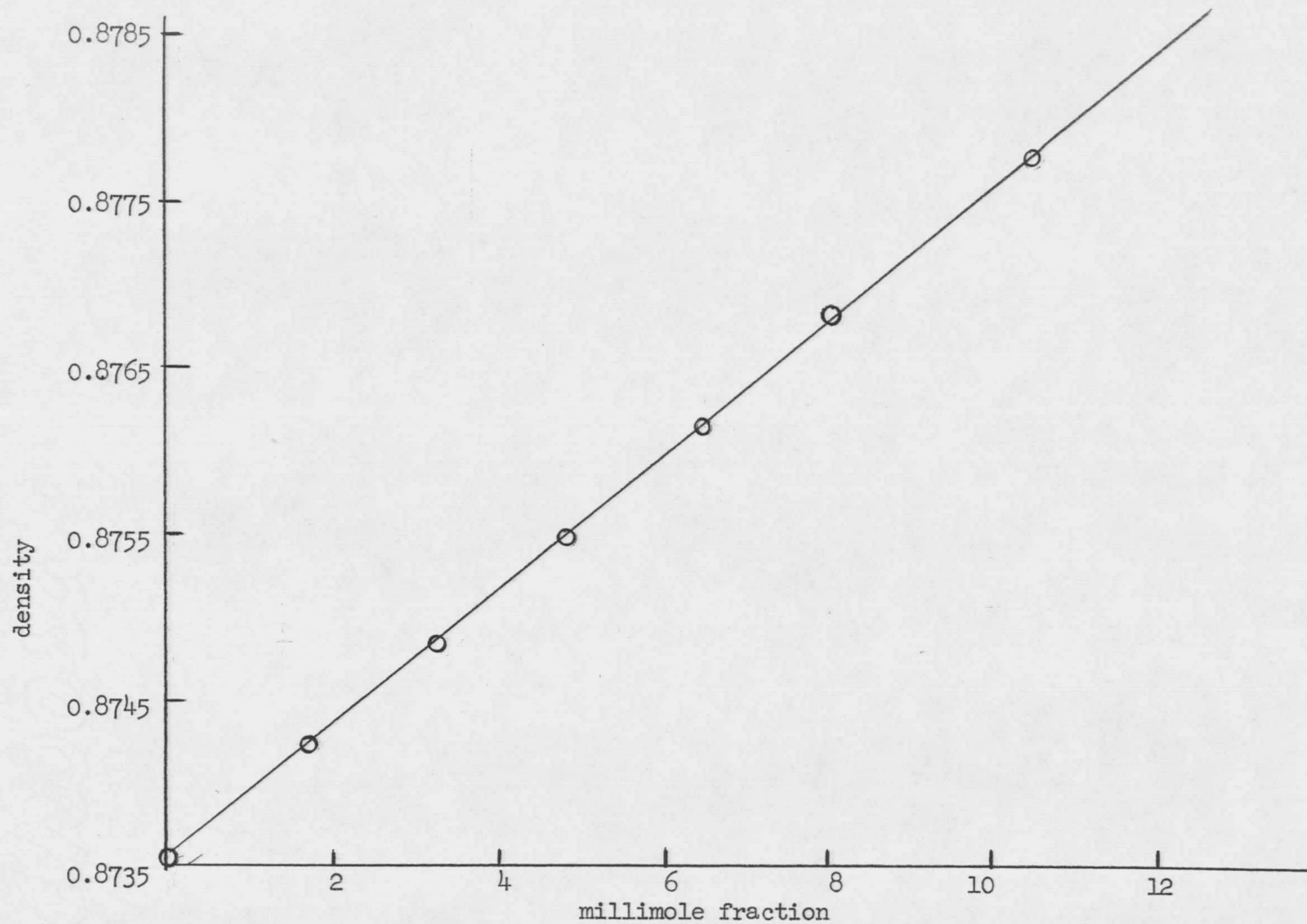
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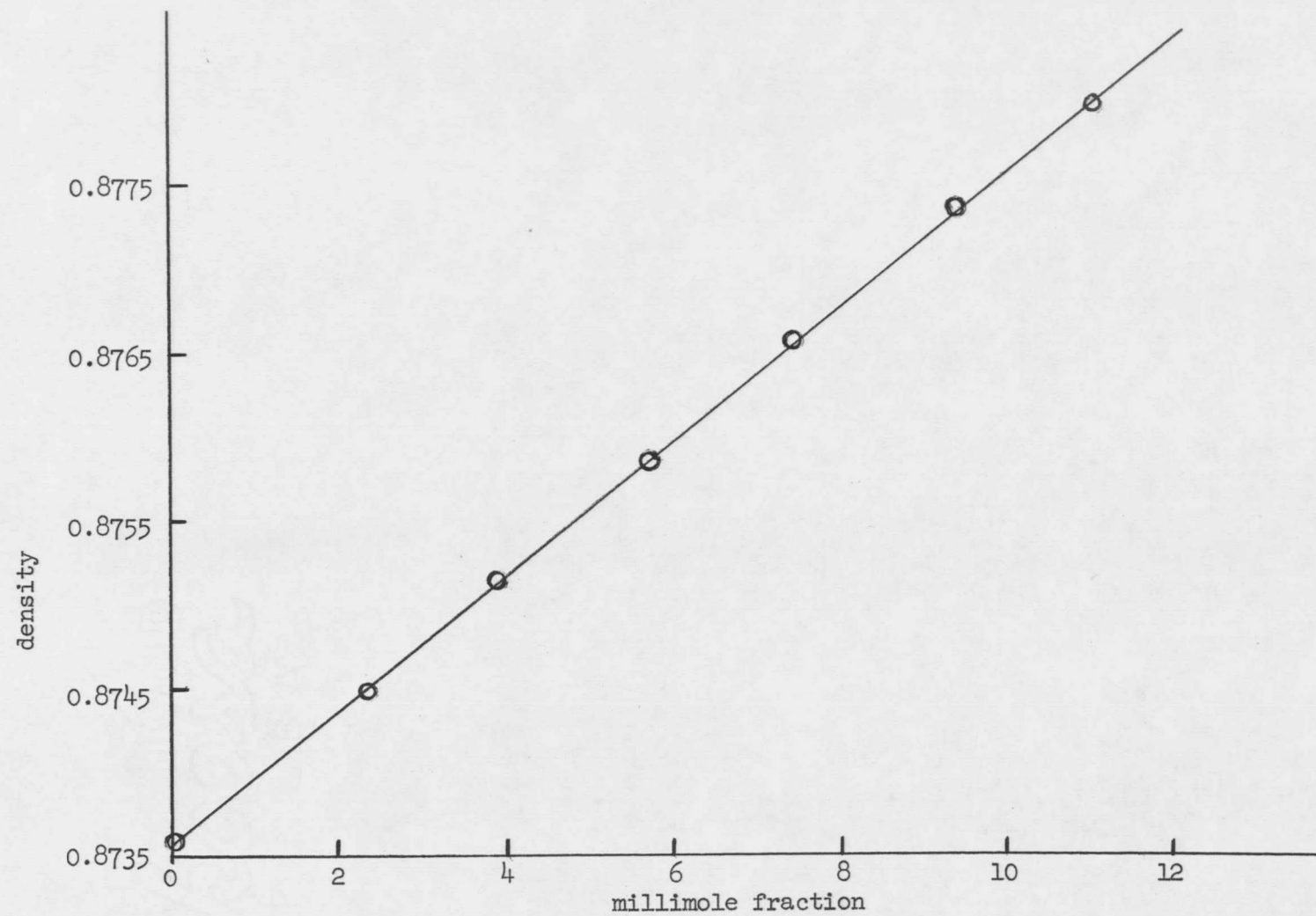
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density vs. millimole fraction ----- n-butyl orthovanadate

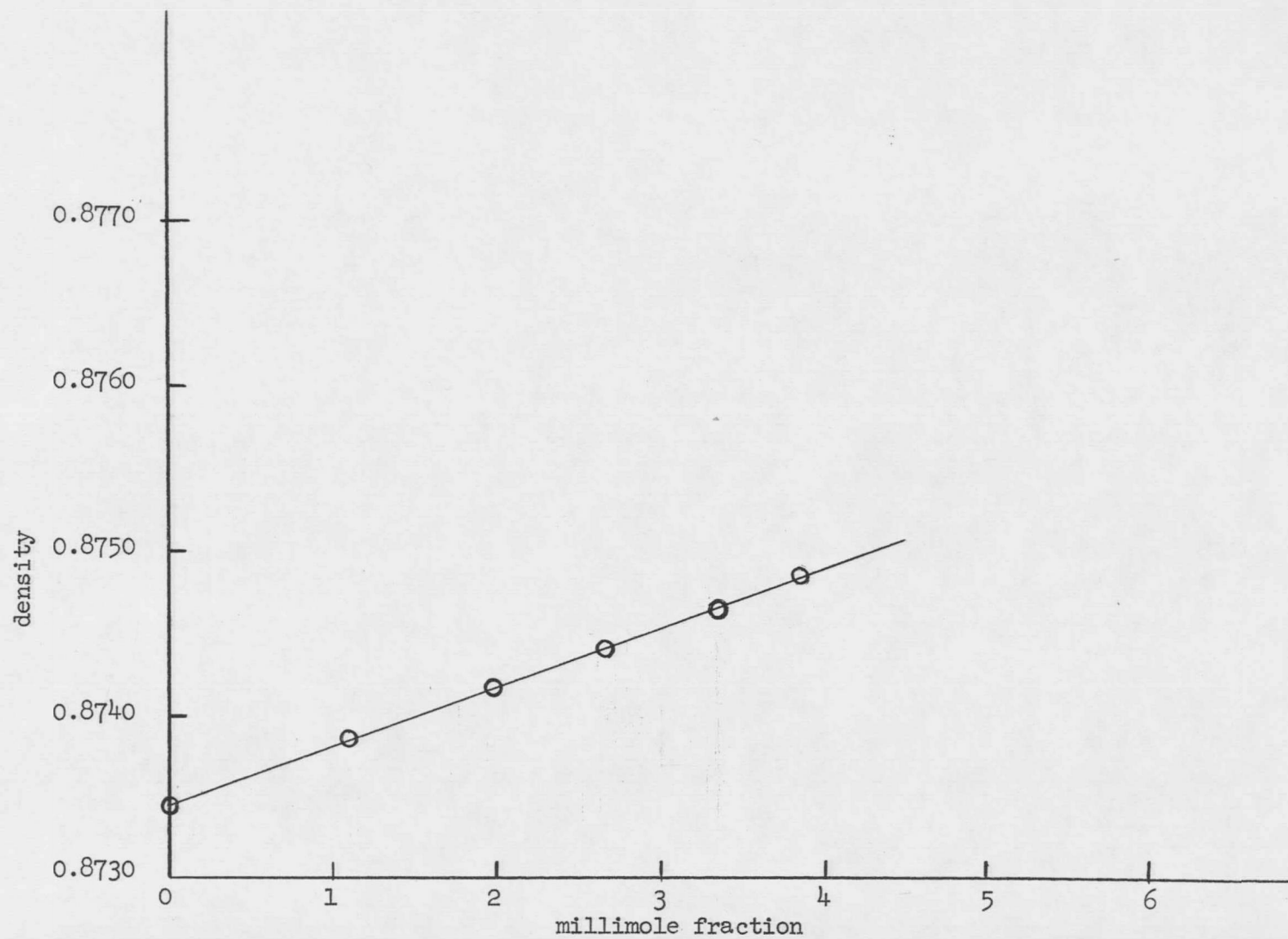


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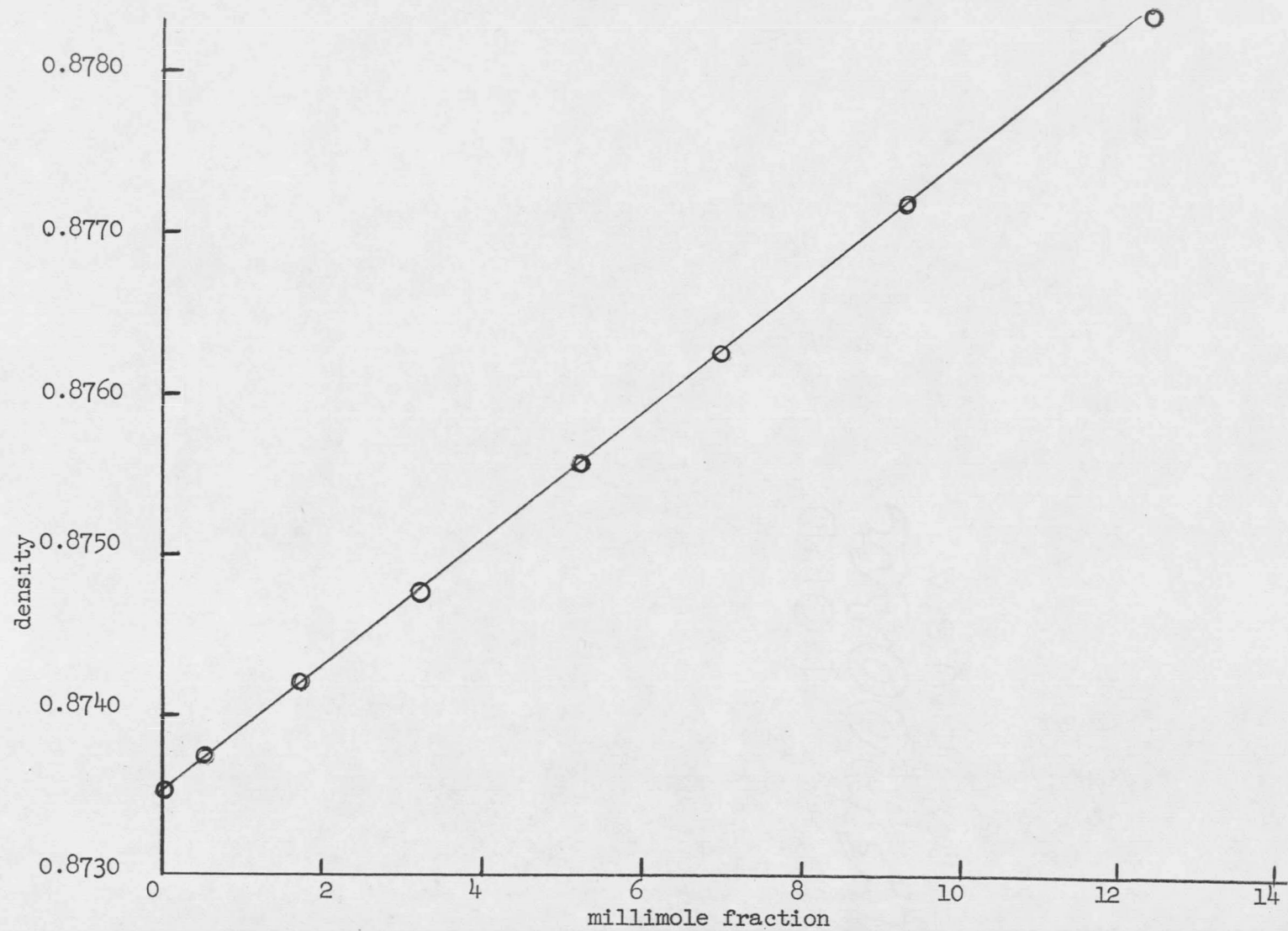


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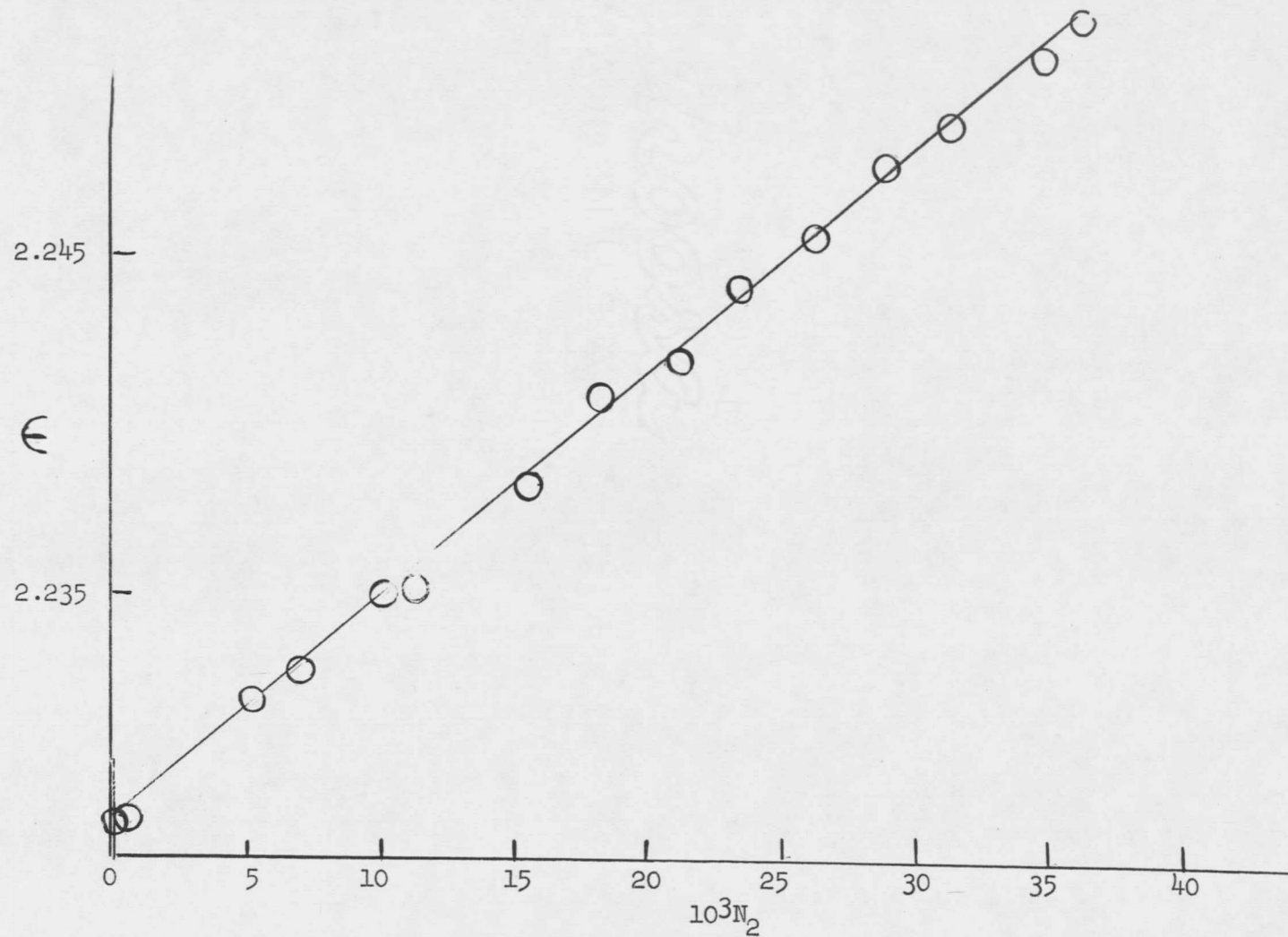
density vs. millimole fraction ----- sec-butyl orthovanadate



density vs. millimole fraction ----- t-butyl orthovanadate

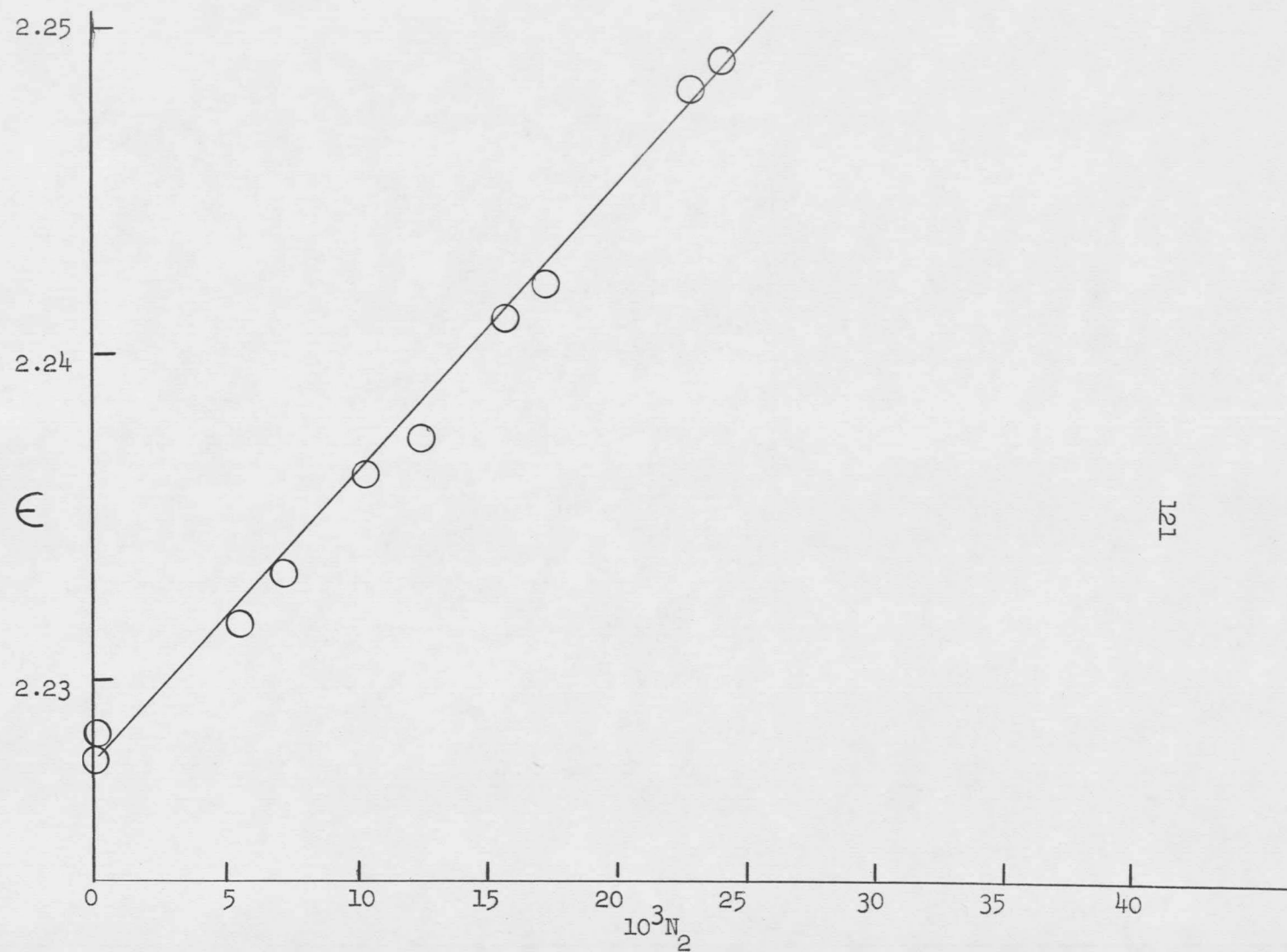


density vs. millimole fraction ----- t-amyl orthovanadate

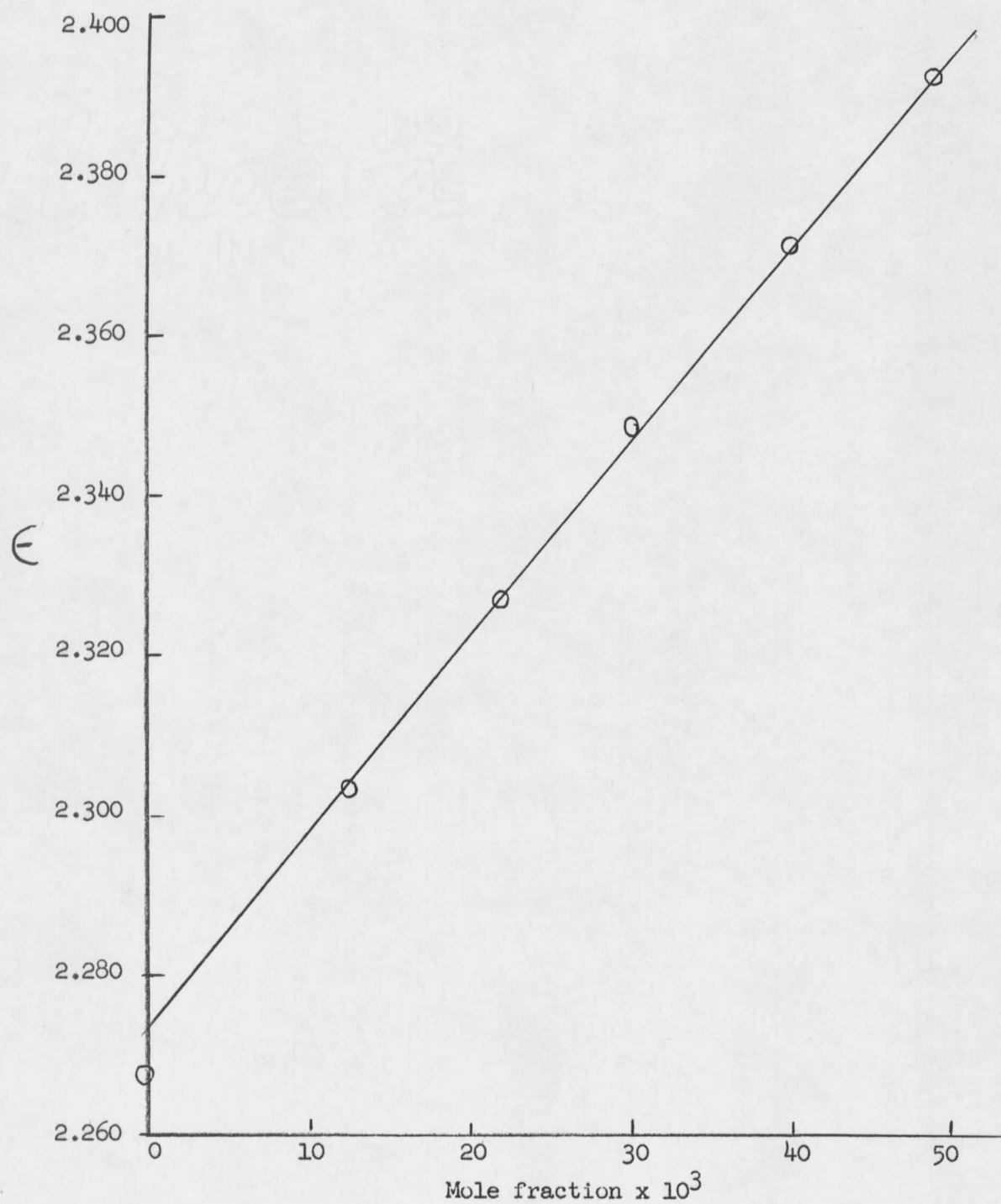


dielectric constant vs. mole fraction

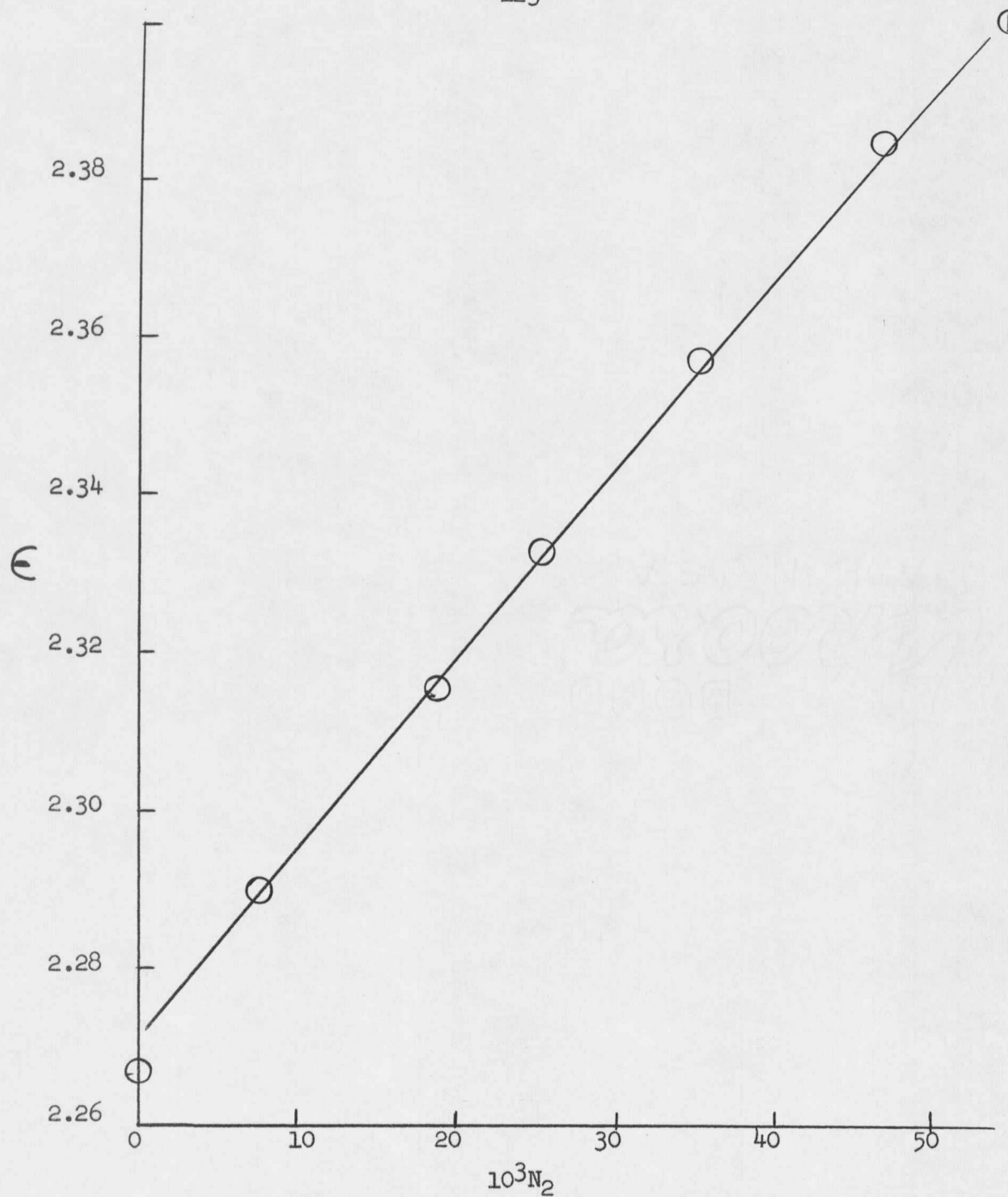
vanadium oxytrichloride



dielectric constant vs. mole fraction
vanadium tetrachloride

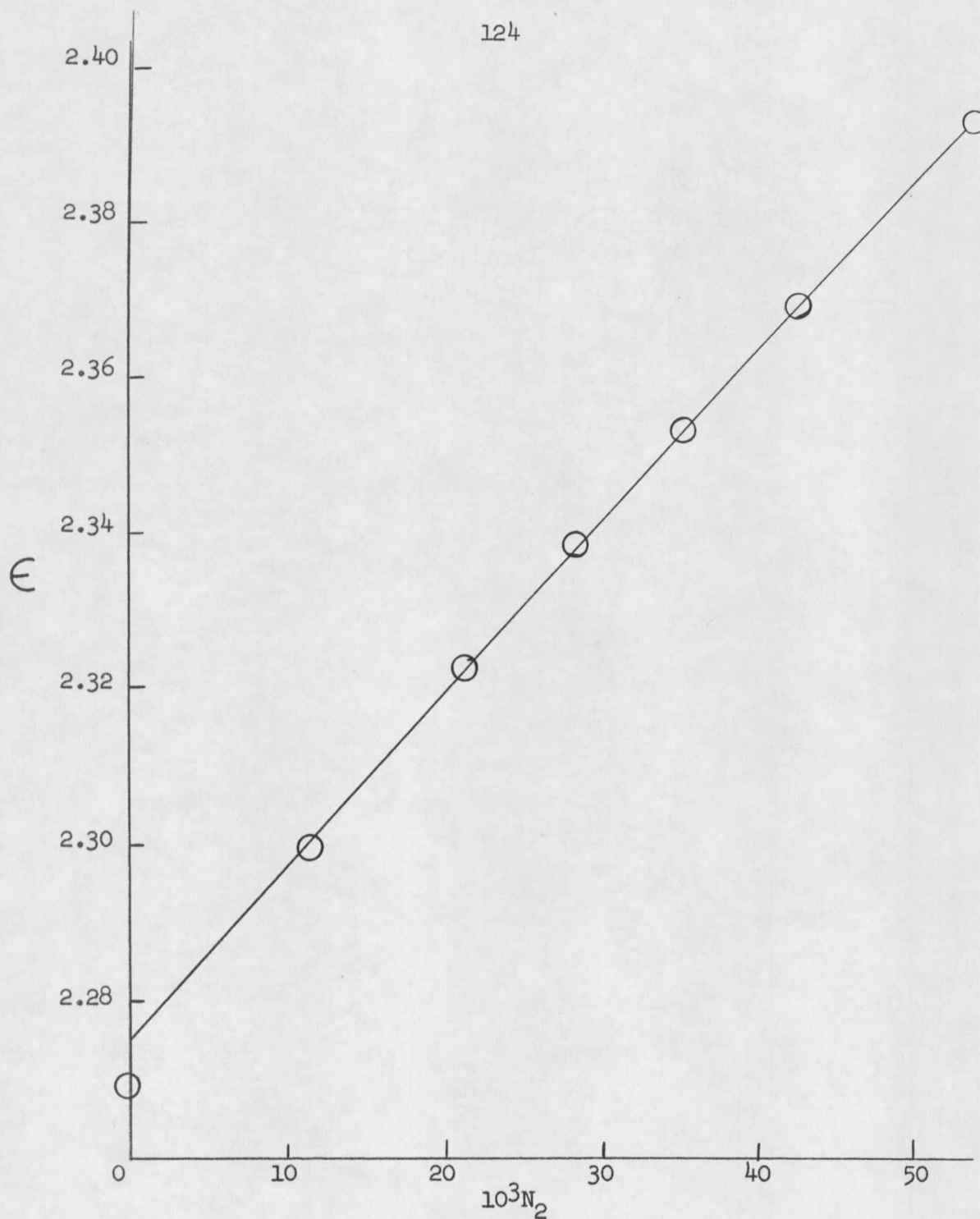


n_D vs. N_2 ---- ethyl orthovanadate



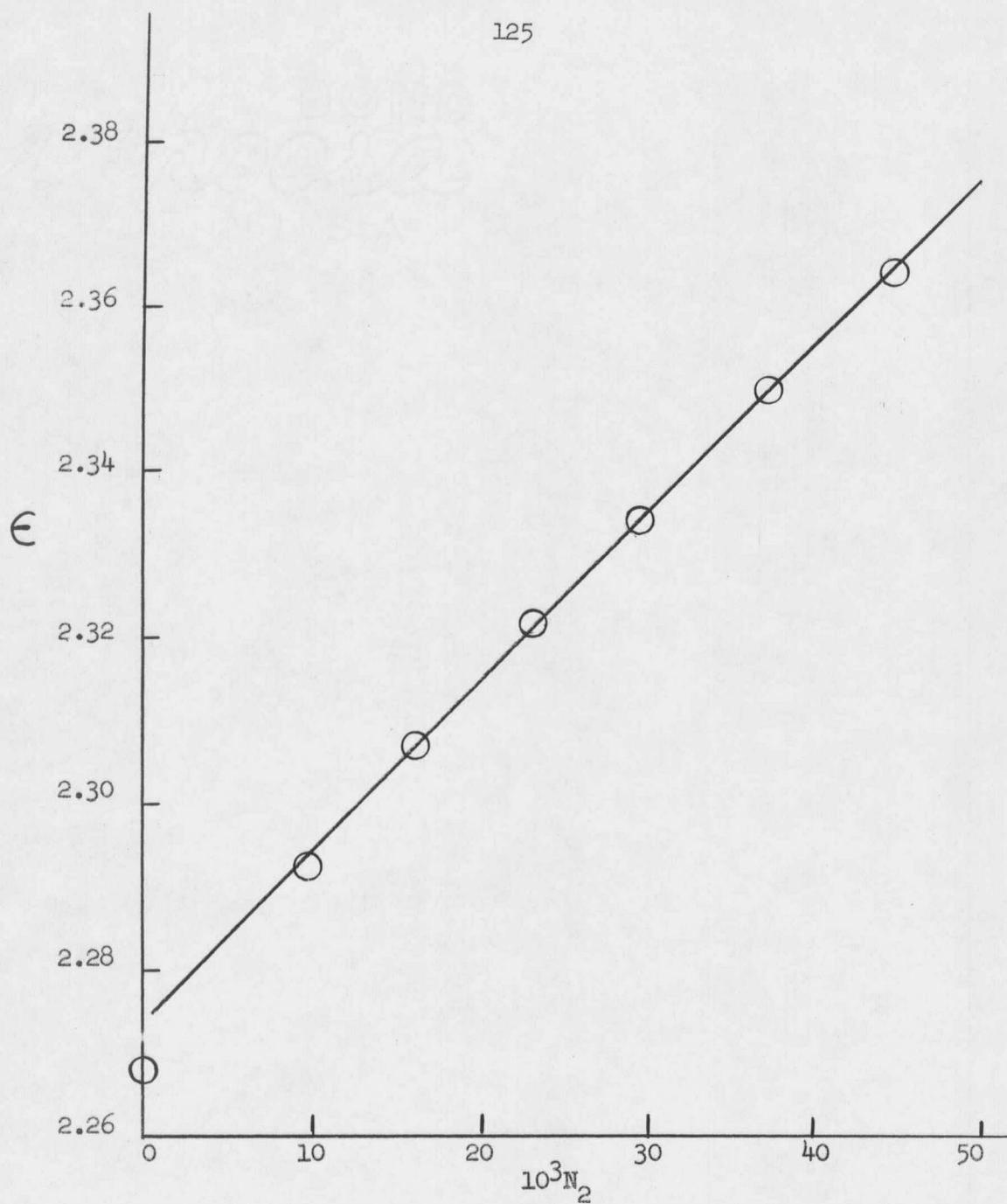
dielectric constant vs. mole fraction

isopropyl orthovanadate



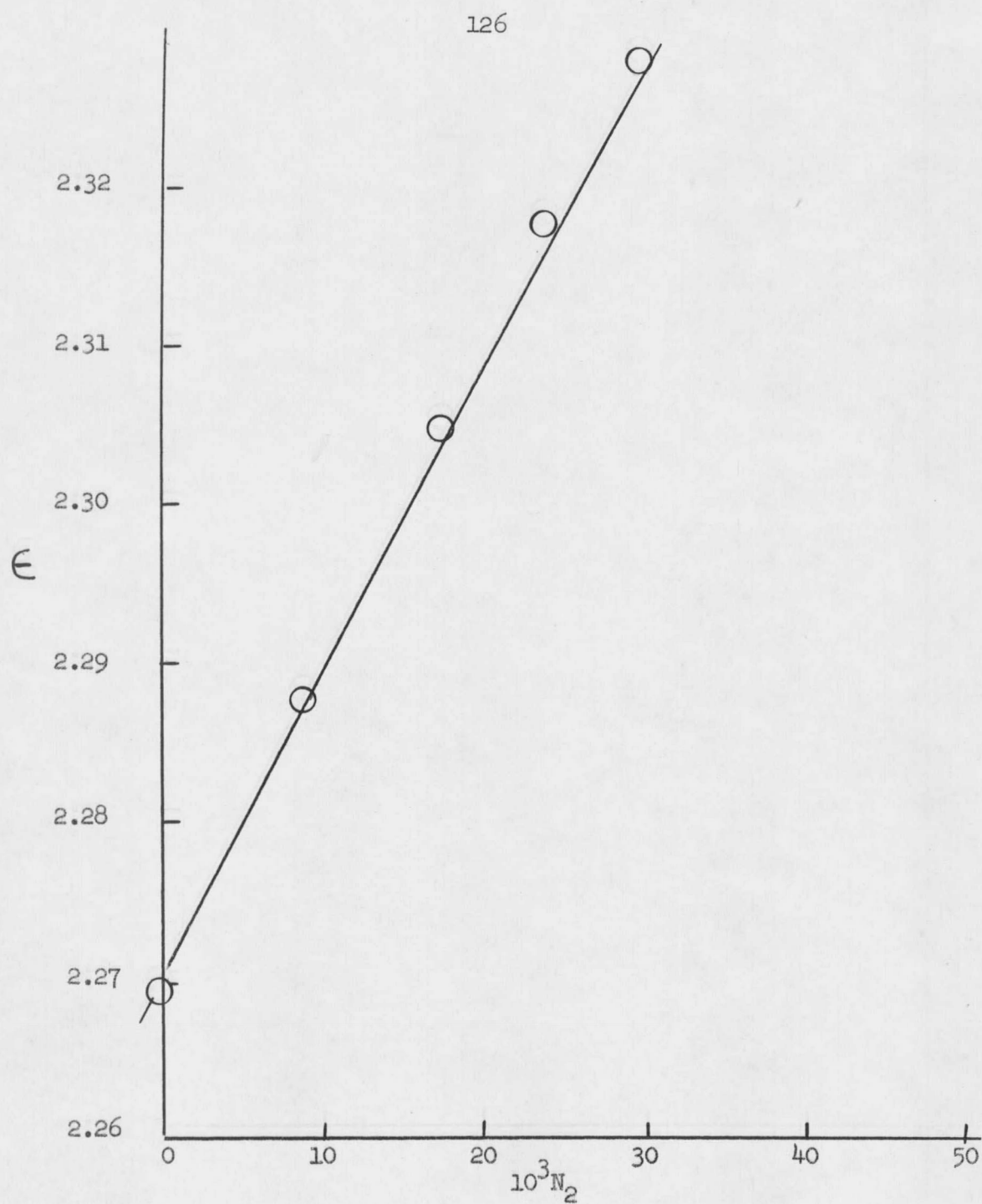
dielectric constant vs. mole fraction

n-propyl orthovanadate



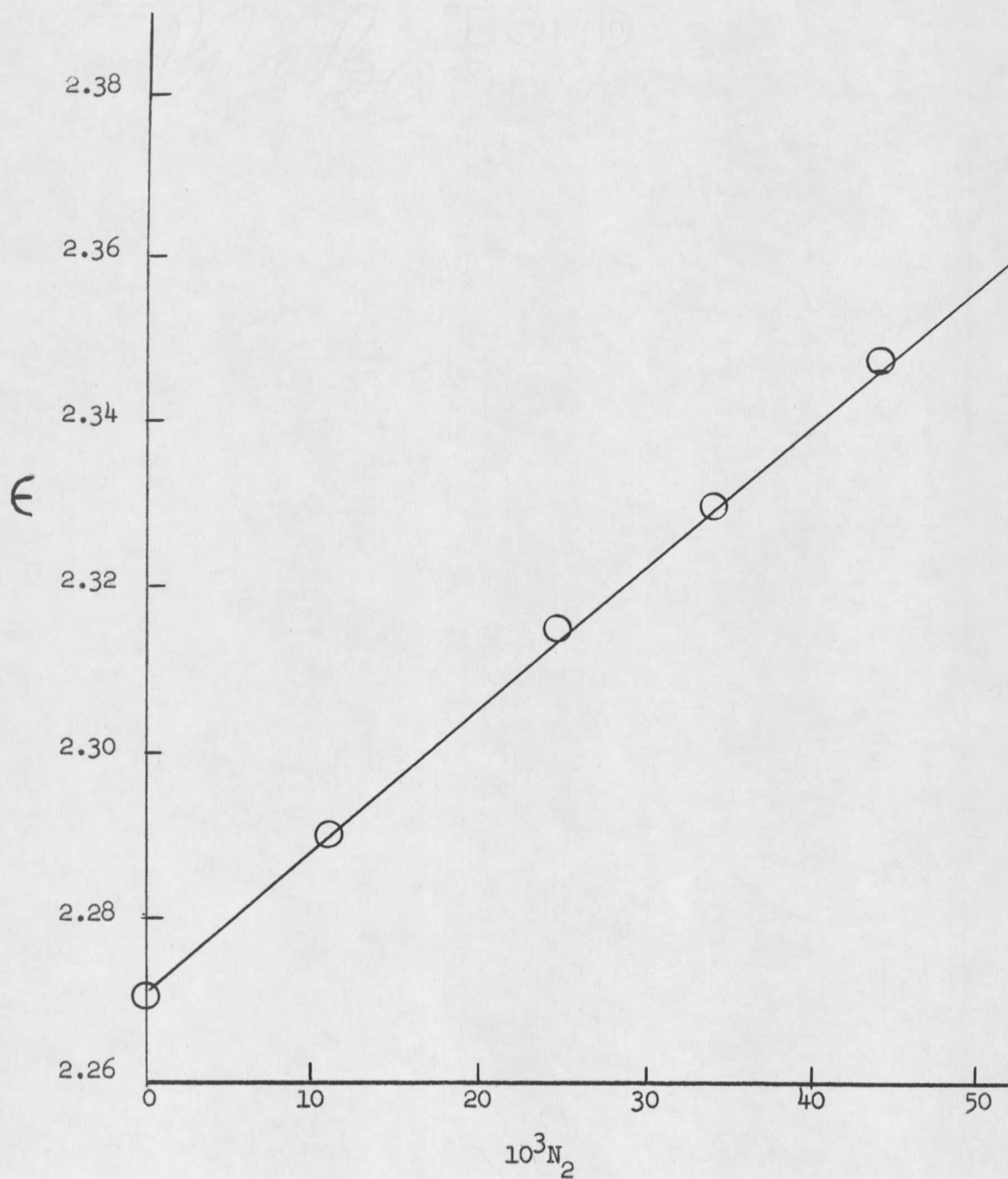
dielectric constant vs. mole fraction

n-butyl orthovanadate



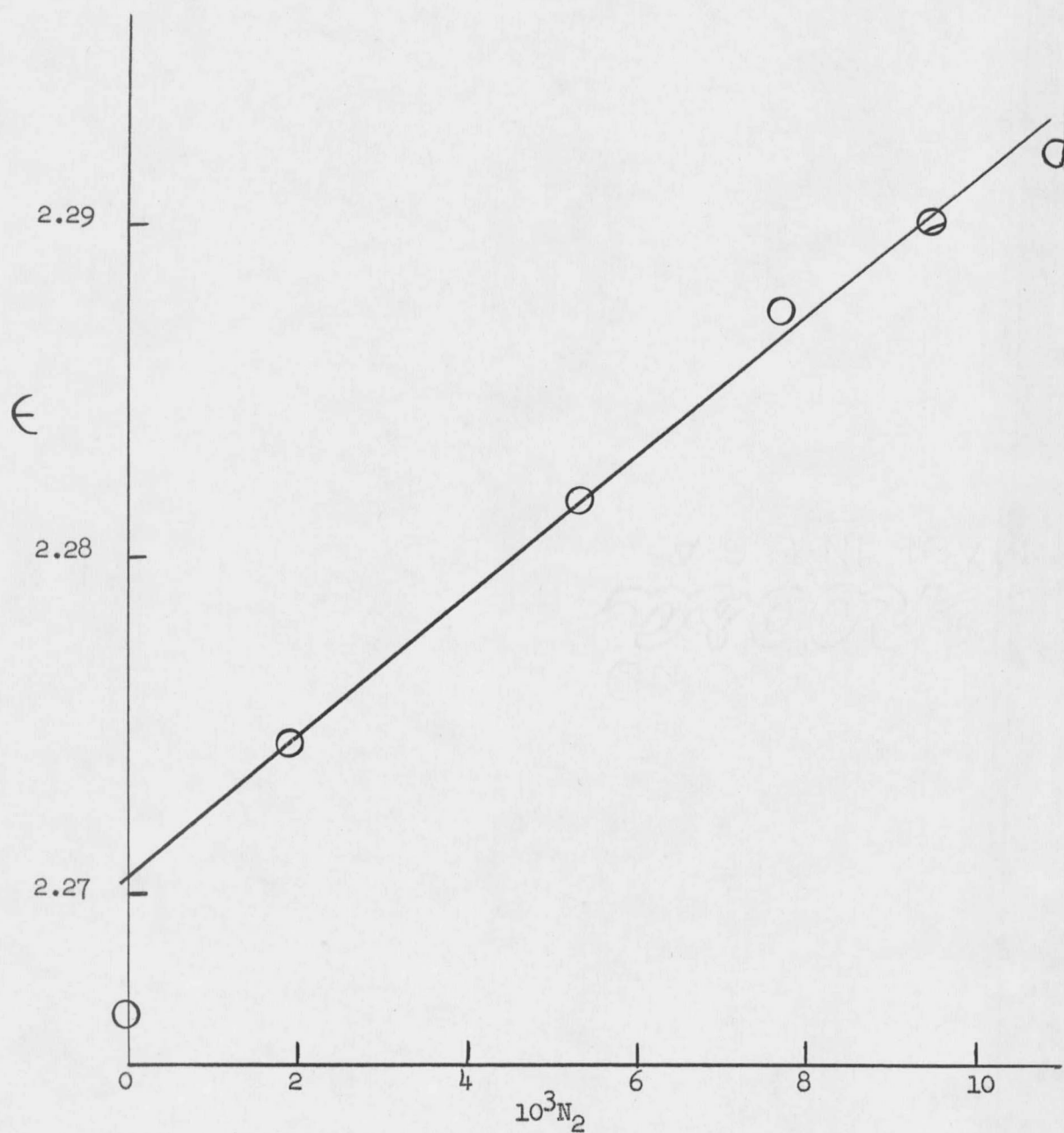
dielectric constant vs. mole fraction

iso-butyl orthovanadate



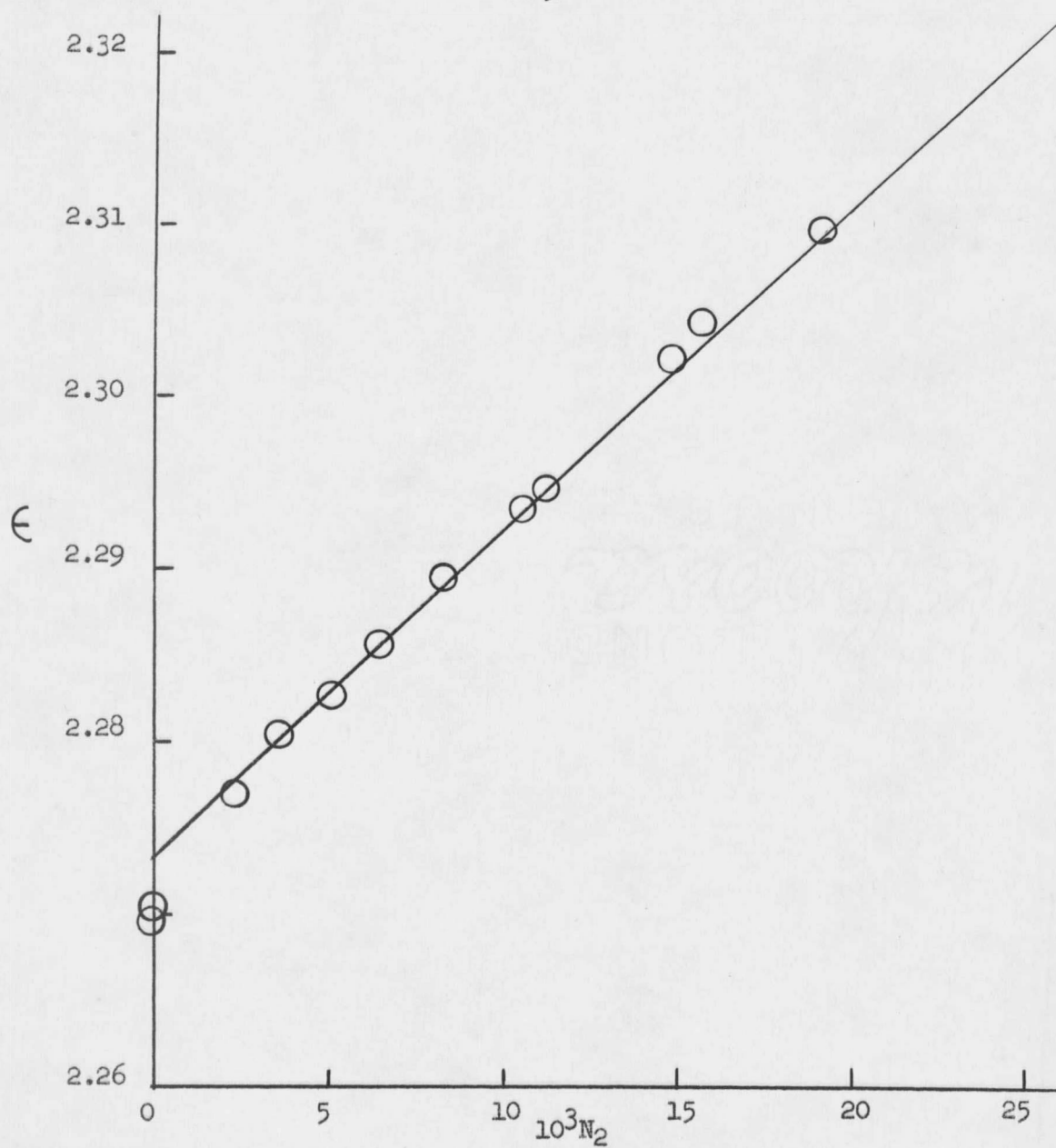
dielectric constant vs. mole fraction

sec-butyl orthovanadate



dielectric constant vs. mole fraction

t-butyl orthovanadate



dielectric constant vs. mole fraction

t-amyl orthovanadate

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