



The viscosity and vapor pressure of orthotitanates and related orthoesters
by Norman J Birkholz

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
© Copyright by Norman J Birkholz (1959)

Abstract:

Viscosities and densities at various temperatures from 0°C to 60°C are reported for ethyl, n-propyl, and n-butyl orthotitanates; for ethyl, n-butyl, and n-heptyl orthosilicates; and for ethyl, n-propyl, n-butyl, and n-amyl orthocarbonates. The preparative method for n-amyl orthocarbonate from NaOEt and chloropicrin is given.

By the method of Tyuzyo, Evis vs. V plots of the orthotitanates, when compared with similar plots of non-aggregated orthosilicates and orthocarbonates, showed the following degrees of aggregation for the pure liquid orthotitanates: Et, 3; n-Pr, 3; n-Bu, 2.

Melting points of ethyl orthotitanate and the orthocarbonates, all of which supercool, were found by intersection of viscosity - temperature curves ($\log \eta$ vs. $1000/T$). The melting point of ethyl orthotitanate was 33.7°C, while those of the orthocarbonates were: Et, 10.850C; n-Pr, 24.66°C; n-Bu, 33.8°C; n-Am, 40.8°C.

Vapor pressures of ethyl and n-propyl orthotitanates were measured by effusion, gas transpiration, and "self-manometer" methods. The vapor pressure of n-butyl orthotitanate by the "self-manometer" is also given.

By extending the use of the Trouton constant to low boiling point pressures, the energies of dissociation of ethyl and n-propyl orthotitanates were found to be 59.7 kcal per mole of trimer at 372°K and 64.5 kcal per mole of trimer at 400°K, respectively. The corresponding Ti...O coordinate bond energies were 10.0 and 10.8 kcal per mole of bonds, respectively, based on six equivalent bonds per trimer.

By interpretation of vapor pressure data, ethyl and n-propyl orthotitanates were found to be essentially monomeric in the vapor phase.

The following special apparatus were constructed: "self-manometer", vacuum dilatometer, effusion cell, gas transpiration cell, and vacuum viscometer (capillary type). Equations for use of the vacuum viscometer are derived.

10988

THE VISCOSITY AND VAPOR PRESSURE OF ORTHOTITANATES AND RELATED ORTHOESTERS

by 55

NORMAN J. BIRKHOIZ

A THESIS

Submitted to the Graduate Faculty

in

partial fulfillment of the requirements

for the degree of

Doctor of Philosophy in Chemistry

at

Montana State College

Approved:

William S. Cook

Head of Major Department

Charles M. Coughlan

Chairman of Examining Committee

Leon Johnson

Dean of the Graduate Division

Bozeman, Montana
January, 1959

TABLE OF CONTENTS

Abstract.....	4
I. Introduction.....	5
II. Viscosity.....	10
A. Experimental materials.....	10
B. Density determinations.....	15
C. Viscometry.....	16
Description of apparatus.....	16
Mathematical discussion of viscometry.....	17
Calibration of viscometers.....	19
Operation of viscometers.....	20
Calculation of viscosities.....	21
Temperature dependence of orthoester viscosities.....	23
Melting points of orthocarbonates and of ethyl orthotitanate.....	23
Activation energies and molar volumes of orthoesters.....	26
Activation energies and molar volumes - literature data.....	27
D. Interpretation of viscosities and discussion.....	28
Melting points of the orthocarbonates.....	28
Viscosities of the orthotitanates.....	29
General discussion of E_{vis} vs. V curves.....	30
Degree of aggregation of orthotitanates.....	32
III. Vapor Pressure.....	34
A. Introduction.....	34
B. Materials.....	34
C. The self-manometer.....	35
D. Vapor pressures by gas transpiration.....	37
E. Effusion vapor pressures.....	40
Introduction.....	40
The effusion apparatus.....	41
Calibration of the effusion cell.....	43
Vapor pressures of orthotitanates by effusion.....	44
F. Comparison of vapor pressure methods and discussion of results.....	45
G. Heats of vaporization and dissociation energies.....	47
H. Structure of orthotitanates.....	53
IV. Summary.....	54
V. Acknowledgements.....	56
VI. Literature cited.....	57
VII. Appendix.....	59
A. Tables	
I. Viscometer calibration equations.....	59
II. Molar volume and E_{vis} of orthoesters at 20°C.....	59
III. Viscosity (calc.) and data for ethyl orthotitanate.....	60
IV. Viscosity (calc.) and data for n-propyl orthotitanate.....	61
V. Viscosity (calc.) and data for n-butyl orthotitanate.....	62
VI. Viscosity (calc.) and data for ethyl orthosilicate.....	63
VII. Viscosity (calc.) and data for n-butyl orthosilicate.....	63
VIII. Viscosity (calc.) and data for n-heptyl orthosilicate.....	63

IX. Viscosity (calc.) and data for ethyl orthocarbonate.....	64
X. Viscosity (calc.) and data for n-propyl orthocarbonate.....	65
XI. Viscosity (calc.) and data for n-butyl orthocarbonate.....	67
XII. Viscosity (calc.) and data for n-amyl orthocarbonate.....	67
XIII. Least squares viscosity equations for orthoesters.....	68
XIV. E_{vis} and V for aldehydes and nitriles at 20°C.....	69
XV. E_{vis} and V for n-alkanes, n-alkyl bromides, and n-alkanethiols at 20°C.....	69
XVI. E_{vis} and V for tetra-alkylsilanes at 20°C.....	70
XVII. E_{vis} and V for alkoxysilanes at 35°C.....	70
XVIII. E_{vis} and V for methylsiloxanes at 20°C.....	70
XIX. Melting points of alkyl orthocarbonates.....	71
XX. Gas transpiration vapor pressure of ethyl orthotitanate.....	71
XXI. Gas transpiration vapor pressure of n-propyl orthotitanate.....	71
XXII. Calibration of effusion cell with mercury.....	72
XXIII. Calibration of effusion cell with mercuric chloride.....	72
XXIV. Calibration of effusion cell with liquid benzophenone.....	72
XXV. Calibration of effusion cell with rhombic sulfur.....	73
XXVI. Vapor pressures of ethyl orthotitanate by effusion.....	73
XXVII. Vapor pressures of n-propyl orthotitanate by effusion.....	74
XXVIII. Trouton constants at various pressures.....	75

B. Figures

1. Dilatometer apparatus.....	76
2. Vacuum viscometer.....	77
3. Self-manometer.....	78
4. Gas transpiration apparatus.....	79
5. Effusion vapor pressure apparatus.....	80
6. Viscosity - temperature curves of orthoesters.....	81
7. Viscosity - temperature curve for benzyl benzoate.....	82
8. Melting point <u>vs.</u> molecular weight of orthocarbonates.....	83
9. E_{vis} <u>vs.</u> V - orthoesters.....	84
10. E_{vis} <u>vs.</u> V - literature data.....	85
11. Vapor pressure of benzophenone by self-manometer.....	86
12. Vapor pressure of ethyl orthotitanate.....	87
13. Vapor pressure of n-propyl orthotitanate.....	88
14. Vapor pressure of n-butyl orthotitanate.....	89
15. Variation of Trouton constant with log P.....	90

ABSTRACT

Viscosities and densities at various temperatures from 0°C to 60°C are reported for ethyl, n-propyl, and n-butyl orthotitanates; for ethyl, n-butyl, and n-heptyl orthosilicates; and for ethyl, n-propyl, n-butyl, and n-amyl orthocarbonates. The preparative method for n-amyl orthocarbonate from NaOEt and chloropicrin is given.

By the method of Tyuzyo, E_{vis} vs. V plots of the orthotitanates, when compared with similar plots of non-aggregated orthosilicates and orthocarbonates, showed the following degrees of aggregation for the pure liquid orthotitanates: Et, 3; n-Pr, 3; n-Bu, 2.

Melting points of ethyl orthotitanate and the orthocarbonates, all of which supercool, were found by intersection of viscosity - temperature curves ($\log \eta$ vs. $1000/T$). The melting point of ethyl orthotitanate was 33.7°C, while those of the orthocarbonates were: Et, 10.85°C; n-Pr, 24.66°C; n-Bu, 33.8°C; n-Am, 40.8°C.

Vapor pressures of ethyl and n-propyl orthotitanates were measured by effusion, gas transpiration, and "self-manometer" methods. The vapor pressure of n-butyl orthotitanate by the "self-manometer" is also given.

By extending the use of the Trouton constant to low boiling point pressures, the energies of dissociation of ethyl and n-propyl orthotitanates were found to be 59.7 kcal per mole of trimer at 372°K and 64.5 kcal per mole of trimer at 400°K, respectively. The corresponding $Ti...O$ coordinate bond energies were 10.0 and 10.8 kcal per mole of bonds, respectively, based on six equivalent bonds per trimer.

By interpretation of vapor pressure data, ethyl and n-propyl orthotitanates were found to be essentially monomeric in the vapor phase.

The following special apparatus were constructed: "self-manometer", vacuum dilatometer, effusion cell, gas transpiration cell, and vacuum viscometer (capillary type). Equations for use of the vacuum viscometer are derived.

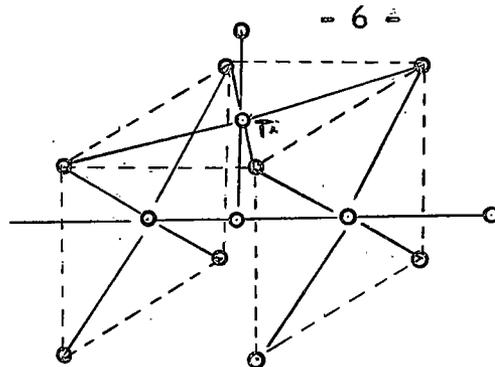
I. INTRODUCTION

The primary objective of this research was the determination of the degree of aggregation of alkyl orthotitanates in the liquid phase. A secondary objective was the calculation of coordinate bond energies in the polymeric materials.

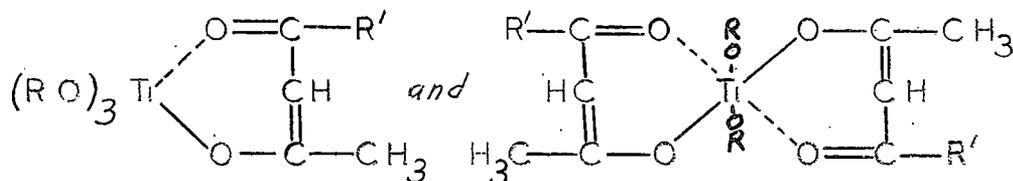
The method of approach for determining the degree of aggregation was by using viscosity data and Tyuzyo's method of calculation (39). Bond energies were calculated from vapor pressure data. Before discussing these methods, however, I will briefly review what is already known about alkyl orthotitanates.

All of the alkyl orthotitanates, with two exceptions, are apparently viscous liquids at room temperature. The exceptions are methyl orthotitanate, which is a high melting solid, and ethyl orthotitanate, which forms a stable solid melting at 34°C . The solid ethyl orthotitanate may be obtained with difficulty either by very slow crystallization at room temperature (several months standing) or by slow warming of the glass formed at -80°C . All of these esters hydrolyze easily and decompose or disproportionate at temperatures below their normal boiling points.

Gaughlan, et al. (10) found that these esters reach an apparent maximum degree of aggregation of 3 in dilute benzene solution. Accordingly, they postulated two structures, one of which is shown on the next page. In both structures titanium was permitted to coordinate to oxygen so that each titanium was surrounded by six oxygen atoms.



Yamamoto and Kambara (43) have made this structure somewhat more plausible by isolating both 5- and 6-coordinate esters such as the following:



(R = Et, n-Pr, or n-Bu; R' = Me or OEt.)

A thorough search of the literature showed that although viscosity is related to liquid structure, no one has yet succeeded in obtaining a satisfactory relationship for complex molecules. The methods which use rheochor (analogous to parachor) are useless. This becomes obvious if one tries to compute the molecular weight of an acid, e. g. acetic acid, from either parachor or rheochor. In either case, empirical "structure" constants must be included to account for the "carboxylic acid group". The molecular weight calculated on this basis will always be that of the monomer. Several methods of relating viscosity to structure by group additivities were examined and found to be of no help for the same reason.

It appears that the relationship of Eyring (17) is still perhaps the most useful. The simplified form of the equation is as follows:

$$\eta = \frac{Nh \exp \Delta F^*/RT}{V}$$

η = viscosity
 N = Avogadro's number
 h = Planck's constant
 V = molar volume
 R = gas constant
 T = absolute temperature
 ΔF^* = free energy of activation for viscous flow.

Calculations from this equation give reasonable viscosities, but the reverse process of calculating molecular weights yields values correct only in order of magnitude. Mackenzie's recent modification (26) of this equation seemed promising until calculations showed that it led to molecular weights smaller than unity for orthotitanates.

Bondi (6) presents very good evidence that molecules of equal molecular weight and similar shape have equal viscosities. He was able to compare viscosities of carboxylic acids and alkanes or esters in this way. For instance, the molecular weight of dimeric valeric acid is 204 and that of tetradecane is 198. The viscosity at 20°C is .022 poise for both compounds.

Hugel (22) presents data on the viscosity of SnR_4 and PbR_4 compounds, from which it appears that the ratio of viscosities is roughly equal to the ratio of molar volumes.

Tyuzyo (39), whose method is utilized in this thesis, found that a plot of E_{vis} , activation energy of viscous flow, vs. molar volume yields a smooth curve for n-paraffins. By finding the point at which the horizontal line from the E_{vis} of some other compound intercepts the curve, a new volume is obtained which is the volume of the unit of flow in the liquid. This volume divided by the observed molar volume of the liquid gives the

degree of aggregation of the liquid. A large number of carboxylic acids gave degrees of aggregation of 2.0 to 2.4, which seems to validate the method. Data for HCN and HF also yielded values in agreement with those from other methods.

The use of Tyuzyo's n-paraffin curve for molecules of different shape does not seem to be justifiable. Whereas dimeric carboxylic acids would have the same general shape as n-paraffins, orthoesters would not. Also, long-chain molecules may flow by using only a fraction of their volume in the process of activation. This would have the effect of giving a value for E_{vis} which would not reflect the unit volume of flow for any molecules except those of similar shape.

Therefore, a new curve was needed as a standard to replace the n-paraffin curve, and it seemed reasonable that compounds of the type $C(OR)_4$ and $Si(OR)_4$ would be satisfactory substitutes. Both of these should be monomeric liquids.

Some uncertainty arises in the determination of E_{vis} . According to the equation

$$\ln \eta = E_{vis}/RT + \text{constant},$$

E_{vis}/R represents $d(\ln \eta)/d(1/T)$, the slope of a curve. Jobling and Lawrence (24) have found this slope at constant pressure to be far different from that at constant volume. Only at high pressures do the two slopes converge. The convention adopted in this thesis will be to represent E_{vis} by $R d(\ln \eta)/d(1/T)$ at constant pressure. Since I will be dealing with empirical functions on a comparative basis only, the only real objection to this may be that this E_{vis} may not be a true measure of activation energy

of viscous flow. Since no author has yet succeeded in defining this term unequivocally, I am no worse off for such an arbitrary definition.

The bond energy of the Ti - O.....Ti coordinate bonds of orthotitanates may be calculated from vapor pressure data. Vapor pressure variation with temperature gives rise to an enthalpy change which involves enthalpies of both dissociation and vaporization. The enthalpy of vaporization can be evaluated from Trouton's rule. This allows calculation of enthalpy of dissociation.

The determination of vapor pressure - temperature functions for the orthotitanates may also be used to evaluate the vapor density. Effusion and gas transpiration methods of vapor pressure determination could be used for vapor pressure and molecular weight determination if both sets of experimental values were of equal precision. This condition was not satisfied in this work, but comparison with a third method of vapor pressure measurement has permitted qualitative evaluation of the vapor phase molecular weight.

II. VISCOSITY

A. Experimental materials

Halides

Chloropicrin, $TiCl_4$, and $SiCl_4$ were reagent grade materials.

Alcohols

Ethanol, n-propanol, n-butanol, n-pentanol, and n-heptanol were carefully refractionated. Fractionation in each case was regulated to insure anhydrous, non-isomeric alcohols.

Ethyl orthotitanate

Ethyl orthotitanate was prepared by reaction of stoichiometric quantities of $TiCl_4$ and NaOEt in ethanol (about 30 g. Na per liter). The $TiCl_4$ was added slowly (2-3 hours) to the alkoxide solution maintained at $10^\circ C$. Stirring was maintained for 2-3 hours longer while the slurry was being refluxed. After overnight standing, the mixture was centrifuged and the solvent distilled off under vacuum. The ester was purified by fractionation through a 10" Vigreux column. It was not analyzed for titanium, but analysis for chlorine - nitric acid digestion followed by $AgNO_3$ - was only faintly positive. Densities: $d^{20.00}$ 1.10915 and 1.10928; $d^{60.00}$ 1.07062 and 1.07084. Interpolated densities: d^{25} 1.1044; d^{35} 1.0948. Literature densities: d^{25} 1.1044 (13); d^{35} 1.107 (34). (All densities in g/cc.)

n-Propyl orthotitanate

The method was identical to that described for the ethyl ester. Analysis for chlorine was only faintly positive. Analysis for Ti by nitric acid digestion followed by ignition to TiO_2 gave 16.73 and 16.71% Ti, whereas the theoretical value is 16.83%. Densities: $d^{20.04}$ 1.03924 and

1.03953; $d^{60.00}$ 1.00619; $d^{60.01}$ 1.00645. Interpolated densities:
 d^{25} 1.0353; d^{35} 1.0270. Literature values: d^{25} 1.0329 (13); d^{35} 0.9970
(34).

n-Butyl orthotitanate

The butyl orthotitanate used in this work was obtained as a gift from the DuPont Co. and was purified as necessary by vacuum distillation. Densities: $d^{20.04}$ 0.99836; $d^{20.02}$ 0.99794; $d^{60.01}$ 0.96577; $d^{59.99}$ 0.96577. Interpolated densities: d^{25} 0.9941; d^{35} 0.9860. Literature values: d^{25} 0.9932 (13); d^{35} 0.9927 (34).

Ethyl orthosilicate

The commercially available material was re-fractionated under atmospheric pressure and a middle cut of constant boiling point was taken. The refractive index, $n_D^{20.0}$ 1.3820, agreed with literature values.

n-Butyl orthosilicate

SiCl_4 was added dropwise, with stirring, to a five-fold excess of n-butanol. After overnight standing, the dissolved HCl was removed by vacuum reflux and the solvent was distilled off. The product was then vacuum fractionated through a 10" Vigreux column. Physical constants: $n_D^{20.0}$ 1.4135; $d^{25.00}$ 0.8923; $d^{2.23}$ 0.9127. Interpolated value: d^{20} 0.8966. Literature values: n_D^{20} 1.4128; d^{20} 0.899 (31).

n-Heptyl orthosilicate

To 104 g. cold n-heptanol (representing 20% excess) was added 30.7 g SiCl_4 with stirring. The temperature was gradually raised to room temperature after complete addition. After overnight standing, the mixture was refluxed at 7 mm to remove all HCl. The mixture was distilled through a

10" Vigreux column at 7 mm. After removal of the alcohol the pressure was lowered to 1 mm and the orthosilicate distilled at roughly 200°C.

Nearly 25 g. of n-heptanol was recovered in the distillation, which may be interpreted as nearly quantitative reaction. Chlorine was shown to be absent in the compound by the usual method. Physical constants:

$n_D^{20.0}$ 1.4349; $d^{44.84}$ 0.8620; $d^{19.51}$ 0.8805. Literature value: d^{25} 0.8958 (14).

Ethyl orthocarbonate

The preparative method of Tieckelmann and Post (38) was followed, in which the ester is prepared from NaOEt and Cl_3CNO_2 . The product was vacuum fractionated before use. It had a fragrant odor without olefin character.

Physical constants: $n_D^{20.0}$ 1.3926; $d^{5.85}$ 0.9299; $d^{39.85}$ 0.8942. Literature constants: n_D^{20} 1.3858, d^{20} 1.020 (38); n_D^{20} 1.3864, d^{20} 1.0232 (40).

The infra-red spectrum of the pure liquid showed no peaks characteristic of ethylenic or alkyl carbonate structures. The refractive indices of other authors may be low because of the presence of either ethyl carbonate or degradation products of the ethyl orthocarbonate. Atmospheric fractionation may remove the ethyl carbonate, but serves to break up the orthocarbonate. Support for this view comes from the observation that all of the orthocarbonates have a strong olefin odor when heated at their normal boiling points, and from the low refractive index of ethyl carbonate (n_D^{25} 1.3829 (7)). Also, the boiling points of alkyl carbonates and their orthocarbonate analogs are so close together that simple distillation will not separate them.

n-Propyl orthocarbonate

The method of preparation was similar to that of Tieckelmann and Post (38), but the method of working up the reaction mixture was altered. The method used here was to wash the crude reaction mixture (from about 2 liters n-PrOH, 70 g Na, and 100 g chloropicrin) with one liter of water, then with two 500 ml portions of water. The aqueous fractions were extracted with 200 ml ether, and the combined ether and alcohol portions were vacuum distilled at 10 mm. When about 400-500 ml remained undistilled, a 10" Vigreux column was attached to the distilling flask and the distillation continued until the remaining propanol was removed. The liquid remaining was filtered and fractionated through the Vigreux column at 1 mm. The product did not have any olefinic odor. No alkyl carbonate or ethylenic peaks were found in its infra-red spectrum. Physical constants: $n_D^{20.0}$ 1.4097; b.p. 101°C/13 mm; $d^{22.87}$ 0.8944; $d^{68.94}$ 0.8513. Literature constants: n_D^{20} 1.4100; d^{20} 0.897 (38).

n-Butyl orthocarbonate

The preparative method was similar to that of n-propyl orthocarbonate. Yield was 65% of theory - considerably better than literature values. It was odorless and showed no alkyl carbonate or ethylenic peaks in the infra-red spectrum. Physical constants: $n_D^{20.0}$ 1.4216; $d^{47.48}$ 0.8649; $d^{23.57}$ 0.8849. Literature values: n_D^{20} 1.4216; d^{20} 0.8879 (38).

n-Amyl orthocarbonate

This compound has not previously been prepared. In fact, Arbutzov and Vinogradova (2) stated that they could not prepare alkyl orthocarbonates higher than butyl by the chloropicrin method.

The method was essentially the same as outlined for n-propyl ortho-carbonate. The material was vacuum fractionated in an unpacked column containing a Monel spiral at about 0.1 mm condenser pressure. Even at this low pressure, the still pot temperature was so high as to appreciably decompose the ester into an olefin and other unknown degradation products. The distillate had a very strong skunk odor and decolorized bromine in CCl_4 . The ester was further purified by fractionation through a 10" Vigreux column at 0.1 mm. The middle cut from this fractionation was nearly odorless, did not exhibit alkyl carbonate or ethylenic peaks in its infra-red spectrum, and had the following physical constants: $n_D^{20.0}$ 1.4302; $d^{90.12}$ 0.8260; $d^{28.8}$ 0.8768. The refractive index predicted for the compound (from a study of indices of lower orthocarbonates) was 1.431, and that predicted for n-amyl carbonate was 1.421. Carbon-hydrogen analysis found C: 70.3%; H: 12.5%. Theory predicts C: 70.0%; H: 12.30%.

Benzyl benzoate

Commercial benzyl benzoate may contain benzaldehyde, benzyl alcohol, and benzoic acid. These were removed by washing with sodium bisulfite, NaOH, and water in the order named. Mild heating with application of 10 mm vacuum removed the water, and vacuum fractionation through a 10" Vigreux column purified the compound for use as a viscosimetric standard. It should be noted that vacuum fractionation through a packed column raises the distillation temperature high enough to cause degradation.

Sucrose solutions

For use as viscosimetric standards, 40% and 60% sucrose solutions were prepared from analytical grade sucrose and distilled water.

B. Density determinations

Density determinations were made in dilatometers of 10-15 ml capacity. These dilatometers were calibrated with pure mercury at two temperatures, the capillaries having been calibrated with mercury prior to construction. The coefficient of expansion of the glass was calculated from the mercury calibrations. All measurements were corrected for glass expansion and for buoyancy.

The densities of orthosilicates and orthocarbonates were measured in dilatometers open to the atmosphere, whereas those of the orthotitanates were measured in the vacuum dilatometer shown in Fig. 1. A possible source of error occurs here, in that the dilatometers were calibrated at atmospheric pressure, whereas the orthotitanate densities were determined in vacuum. Ordinary thermometers may read as much as 0.15° low in an evacuated chamber, which illustrates the effect. Thermometer bulbs are made of thin glass, however, whereas these dilatometers were of considerably thicker material, so the error is probably very small.

The method of filling the vacuum dilatometers is illustrated in Fig. 1. By means of suitably placed stopcocks, the distilled alkoxide is forced into the dilatometer until sufficient liquid rises in the center capillary. This capillary is then sealed off under vacuum. Excess liquid is boiled out of the side capillary and it is also sealed off under vacuum. Some decomposition occurs during the sealing-off process, but not enough to affect the results.

The sealed dilatometer is placed in a thermostat accurately held to 0.01° and the relative height of liquid in the capillaries is measured by a

cathetometer. Following such a determination, the dilatometer may be broken open at the vacuum seals and re-used several times until the capillaries have become too short.

The measured densities are reported in the section describing materials. In most cases there is good agreement with literature values where such are available. I disagree with the densities of Speer (34), but assume his values were primarily for characterization, not for use as accurate physical constants.

G. Viscometry

Description of apparatus

A new method and apparatus were developed for measurement of viscosity in vacuum. This was necessitated by the ease with which the titanium orthoesters hydrolyze. The apparatus is illustrated in Fig. 2. Several viscometers were used, differing in length and bore of capillary, relative height of capillary endings, and bulb volume. These differences were introduced deliberately to provide convenient flow times. Those viscometers having long capillaries had to have many bends in the capillary tubing to keep the viscometers compact.

Since the time of flow is dependent on changes in positioning of the viscometer which affect the pressure head inside, all viscometers were rigidly supported by a system of clamps on a ringstand bolted to the floor of the thermostat. The thermostat was controlled to 0.01° by a sensitive thermoregulator.

Each viscometer was calibrated with reference liquids before final assembly. The construction of the viscometer during calibration is shown

in Fig. 2a. The details of calibration will be presented following a mathematical discussion of viscometry. After calibration, the tubing is bent at (h) in order to bring the free ends together and the loop is sealed. The joint is carefully softened while the viscometer is in its vertical position so as to anneal the joint and remove strains which might affect the calibration geometry. The extra glass shown in the finished viscometer is then sealed on at (f). The narrow tubing at (d) is thickened 8 mm stock. The large tubing is 15 - 20 mm, tubing from (b) to (c) is 8 mm, and the capillary bore is variable (ca. 1 mm or less). Tubing at points (a) and (b) is capillary. Overall height and weight of a typical viscometer were 15 inches and 150 grams.

Mathematical discussion of viscometry

Since this is a new instrument, mathematical treatment of the method had to be developed also. This treatment was designed to permit a given liquid to be vacuum distilled into the apparatus and to permit measurement of its viscosity over a temperature range without re-opening the viscometer.

Poiseuille's equation for flow of liquid through a capillary may be written

$$\eta = \pi Pr^4 \theta / 8VL$$

η = viscosity

P = driving pressure

r = capillary radius

θ = time required for volume, V , to flow

L = capillary length.

For a certain viscometer, this reduces to $\theta = k/P$, where k is a constant. But $P = dgh$, where d = density, g = gravitational acceleration, and h = height of the liquid column giving rise to the pressure, P . Therefore,

$\theta \equiv k/dgh \equiv c/h$, where c is a new constant. If we now let $h \equiv h_0 + \Delta h$, where h_0 is the height of liquid at some reference time θ_0 and Δh is the height above this reference, $\theta \equiv c/(h_0 + \Delta h)$. Since the viscometer has a uniform cylindrical cross section in the region where we will measure Δh , we may write $\Delta h \equiv \Delta V/\pi R^2$, where R is the cylindrical radius. Since density is defined as $d \equiv W/V$, we may say that $\Delta V \equiv \Delta W/d$, where V is the volume, and W is the weight of that volume of liquid. Therefore,

$\theta \equiv c/(h_0 + \Delta W/\pi R^2)$. Letting $\Delta W \equiv W - W_0$, where W_0 and ΔW correspond to h_0 and Δh , respectively,

$$\theta \equiv c/(h_0 + (W - W_0)/\pi R^2)$$

Since all but θ and W are constants, this may be simplified into the following expression where a and b are constants:

$$\theta \equiv a/(b + W)$$

The constants in this expression are then characteristic of a certain liquid in a certain viscometer at a fixed temperature. W is the weight of liquid contained in the viscometer and θ is the time required for a given volume of liquid to flow through the viscometer between fixed points.

For determination of the constants in this equation, various weights of a calibration liquid may be placed in the viscometer and the times of flow at constant temperature recorded. By plotting $1/\theta$ vs. W , a straight line is obtained. The equation of this line may then be found by the method of least squares.

Since it is desirable to calibrate the viscometer at only one temperature but use it at other temperatures without re-calibration, it is necessary to show that no correction need be made for the effect of temp-

erature expansion of the glass used in construction. To do this, we may write the following, where α = coefficient of linear expansion of glass and subscripts refer to two different temperatures:

$$r_1^4 = r_2^4(1 - \alpha \Delta t)^4$$

$$L_1 = L_2(1 - \alpha \Delta t)$$

$$V_1 = V_2(1 - \alpha \Delta t)^3.$$

Then we may use the Poiseuille equation to write the following:

$$\frac{\eta_2}{\eta_1} = \frac{P_2 \theta_2 r_2^4 V_1 L_1}{P_1 \theta_1 r_1^4 V_2 L_2}$$

Upon substituting into this equation the equations for temperature expansion and simplifying, we obtain

$$\frac{\eta_2}{\eta_1} = \frac{P_2 \theta_2}{P_1 \theta_1},$$

which is independent of any coefficient of thermal expansion terms!

Actually, the viscometer will be very slightly temperature dependent, since expansion of the glass due to change of temperature will permit the liquid levels within to rise or fall. This will affect the driving pressure, but the effect is certainly too minute to be of concern here.

Calibration of viscometers

The liquids selected for calibration were water, benzyl benzoate, 40% sucrose solution, and 60% sucrose solution. Bingham and Jackson (3) give the following constants for sucrose solutions: 60%; d^{40} 1.27615, d^{25} 1.28399, η^{40} 21.28 cp, η^{25} 43.86 cp. 40%; d^{25} 1.17439, η^{25} 5.187 cp. Bingham and Sarver (4) give the following for benzyl benzoate: d^{40} 1.0780,

η^{40} 5.243 cp. The data for water were taken from the International Critical Tables (45): d^{35} 0.99406, d^{30} 0.99567, $d^{27.5}$ 0.99640, η^{35} 0.7225 cp, η^{30} 0.8007 cp, $\eta^{27.5}$ 0.8452 cp.

To calibrate a viscometer, various weights of the calibration liquid were placed therein and the flow times recorded. The viscometer was allowed to stand 30 min. in the thermostat before taking a reading. Flow times ranged from 6 min. to 60 min. depending on the liquid and the temperature.

Time was measured by a stopwatch to the nearest 0.1 second. A check over 12 hours against the time signal of radio station WWV showed no error in the watch.

A total of five different viscometers were used. The calibration equations for each are presented in Table I.

Operation of viscometers

Before filling, the viscometer and distilling apparatus were cleaned thoroughly with hot acid, rinsed with dust-free distilled water, and oven dried. The viscometer was then evacuated while hot to remove water vapor. After several such evacuations, the viscometer was weighed to the nearest milligram and assembled with the distillation apparatus. This consisted of a Claisen flask fitted with thermometer and condenser by ground glass joints sealed with silicone grease. The condenser in turn was jointed to a movable fraction-cutting device which held a flask for forerun and tailings of the distillation, and the viscometer itself. All joints were of the drip-tip variety so that stopcock grease could not touch the liquid. Some of the less viscous liquids crept into the joints, in which cases it was necessary to use Teflon sleeves instead of grease.

The orthoesters were distilled into the viscometers at approximately 1 mm. Ethyl orthocarbonate and orthosilicate were distilled in at 10 mm because of their lower boiling points, and the pressure was lowered to 1 mm before sealing off. After a good middle cut of the distillate had passed into the viscometer, it was sealed off under vacuum (point (d) in Fig. 2). The joint formerly attached to the viscometer was then cleaned and weighed together with the filled viscometer to determine the weight of liquid which had passed in.

Before each run, the viscometer had to be flamed dry from (e) to (c) in the diagram (going counterclockwise). It was then laid on its side in the thermostat for 30 min., then righted and placed in its flow position. The small surge bulb, e-a, gave sufficient time to clamp the instrument in place and prepare to start the stopwatch. Following each run, the procedure was repeated at the next temperature. After all runs had been made with a particular liquid, the viscometer was scratched and broken open with a heated glass rod at (d) and (m), flushed several times with dry alcohol to remove traces of the orthoester, and cleaned and re-sealed for re-use.

The data obtained from the orthoesters are presented in Tables III to XII.

Calculation of viscosities

If the viscosity of the orthoester is near that of the liquid used for calibration, the viscosity may be found from the following expression, where subscripts 1 and 2 refer to orthoester and calibration liquid, respectively:

$$\frac{\eta_1}{\eta_2} = \frac{d_1 \theta_1}{d_2 \theta_2} .$$

The first step in calculation is to find the volume of the orthoester contained in the viscometer at the temperature of the determination. This can be calculated from the weight and density of the orthoester. From the volume of the orthoester, it is now possible to find the time required for flow of an equal volume of the calibration liquid at its own calibration temperature. When this time has been found, solution for the orthoester viscosity is a matter of plugging data into the equation. The following steps may make this more lucid:

1. $W_1/d_1 = V_1$
2. $V_1 = V_2$
3. $W_2 = d_2V_2 = d_2V_1 = W_1d_2/d_1$
4. $\theta_2 = a/(b + W_2) = a/(b + W_1d_2/d_1)$
5. $\eta_1 = \eta_2d_1\theta_1/d_2\theta_2$

If greater accuracy is desired, the two-constant equation may be used:

$$\eta_i = Ad_i\theta_i + Bd_i/\theta_i.$$

This equation requires two calibration liquids to evaluate the constants A and B, whereupon the orthoester viscosity may be obtained by plugging in.

This two-constant equation should in general yield more accurate viscosities, but had the disadvantage of being more laborious, since each point-set of data requires the solution of simultaneous equations. It was found that the application of this equation to the experimental data in preference to the simpler equation gave viscosities differing from the latter in the third significant figure. This is about the limit of reproducibility, however, so that viscosities calculated from the simpler equation should not be discredited.

Viscosities calculated from the data will be found, together with the original flow times, in Tables III through XII.

Temperature dependence of orthoester viscosities

Temperature dependent viscosity equations were calculated for all the orthoesters by the method of least squares. The general equation,

$$\log_{10} \eta = a/T - b + cT,$$

was used. This is an empirical equation justifiable mainly by the ease - comparatively speaking - with which it can be "least squared". The least squares calculations of even this convenient case had to be carried to 20 digits in order to obtain solutions. This in turn meant calculation of four 3x3 determinants, each containing 20 digit operations - a most laborious task. The simpler two-constant equation ($c = 0$) was therefore used where possible, since 10 digit figures were sufficient there.

Table XIII gives the results of these calculations and the temperature ranges over which they were calculated. It should be noted that ethyl orthotitanate and all four of the orthocarbonates are representable by two separate curves, each in a different temperature range. The point at which these two curves intersect is discussed in the next section.

Fig. 6 is a graph of $\log_{10} \eta$ vs. $1/T$ for all the orthoesters studied.

Melting points of orthocarbonates and of ethyl orthotitanate

Supercooled liquids in general show a viscosity-temperature discontinuity at the melting point, although this phenomenon has been noted by only a very small number of authors. Since this effect may be unknown to many readers, a graph of $\log_{10} \eta$ vs. $1/T$ for benzyl benzoate (Fig. 7) has been plotted from the data of Bingham and Sarver as an illustration.

It will be noted that the curve is not straight in the non-supercooled region. This curvature seems to be general for all liquids, although less noticeable in some. The melting point shown on the figure as the intersection of viscosity-temperature lines is identical with that experimentally determined by melting.

To calculate the melting point of a liquid from its temperature dependence of viscosity, it is only necessary to realize that at the melting point the viscosity of both the supercooled and normal liquid is the same. Using the subscripts s and n to indicate supercooled and normal regions of the same liquid, and T_m to indicate the temperature of melting, we have

$$\log_{10} \eta_n = a_n/T_m - b_n + c_n T_m = \log_{10} \eta_s = a_s/T_m - b_s + c_s T_m$$

$$\text{Then } T_m^2(c_n - c_s) + T_m(b_s - b_n) + (a_n - a_s) = 0.$$

This last equation is a quadratic in T_m and may be solved by common methods. Two solutions are possible, but if $c = 0$ only one solution is found.

The melting point of ethyl orthotitanate, obtained in this manner by calculation from the viscosity equations, is found to be 33.7°C , which is in excellent agreement with the value of 34°C reported by Caughlan, et al. (10).

The literature melting point of methyl orthocarbonate, -5.5°C , indicated during the course of this research that the melting points of the higher homologs should be in the range of temperatures available with the experimental equipment. In order to find these melting points, the experimental points were carefully examined to find the break, and experimental points were then taken on both sides of the discontinuity. These discontinuities were easily found by graphing for amyl and butyl ortho-

carbonates, but those of ethyl and propyl orthocarbonates had to be found by least squares calculations. To do this, the region on the graph expected to contain the break was located roughly by visual inspection. Least squares equations were then developed for points on both sides of, but not including, the range of points near the expected melting point. Simultaneous solution of these yielded a value for T_m which was now used as a better approximation. All points on both sides of this new T_m were now included in the least squares calculations, and a second value for T_m calculated. These refined calculations were then found to shift the melting point, and the final shifting of points included in the least squares calculations served to produce a T_m which no longer shifted. In case the final value of T_m was such that too few points were included in either the normal or supercooled region, additional data were taken and the calculations repeated.

Table XIX lists these melting points, and Fig. 8 shows the relationship between m.p. and molecular weight for the orthocarbonate family.

An attempt was made to freeze each of the orthocarbonates in order to obtain verification of these melting points, but all attempts failed.

It should be mentioned that the solution of the three-constant equations yields two values for T_m in the case of ethyl and n-propyl orthocarbonates, whereas the two-constant equations used for other esters yield only one. The extraneous solutions were eliminated by approximating the temperature-viscosity equation in the supercooled region by a two-constant form rather than the three-constant form. This caused one of the melting points to shift somewhat more than the other, and the one which did not

shift appreciably was assumed to be the true melting point. The possibility exists, however, that the discarded values are true and refer to a transition point.

The false melting points were: Ethyl orthocarbonate 20.0°C, n-propyl orthocarbonate 33.9°C. The difference between them, 13.9°, may be compared with the difference between the melting points from Table XIX, 13.8°. The comparison is indeed striking!

Activation energies and molar volumes of orthoesters

As was mentioned in the introduction, calculation of activation energies of viscous flow will be according to the simple, although arbitrary, relationship,

$$E_{vis} = R d(\ln \eta) / d(1/T).$$

Since this is variable with temperature for liquids which are not expressible as linear functions of $1/T$, it is necessary to choose a temperature. The temperature selected for this thesis, 20°C, is completely arbitrary. Some of the data taken from literature sources will not be at 20°C and will merit later explanation.

Molar liquid volume, V , is the experimental volume of one mole of liquid as calculated from molecular weights and densities, assuming the liquid species to be monomeric. Table II lists these values calculated from the experimental data. The values for activation energy have been calculated from the equation for the non-supercooled region, even though the liquid may be supercooled at 20°C. This is mainly done to refer all liquids to the same temperature. The particular choice of 20°C was mainly so that comparison might be more easily made with literature data.

This data is presented in graphical form in Fig. 9.

Activation energies and molar volumes - literature data

In order to make more plausible the general method which will be used here to calculate degree of aggregation, it seemed wise to search the literature for viscosity - temperature equations of homologous series. The data presented in the International Critical Tables are not well suited to the task. Much of it is old and inaccurate, and many values did not agree with those given by recent authors. Several articles were discovered which had the desired information. From one, by Friend and Hargreaves (20), has been taken the information on aldehydes and nitriles. Values for E_{vis} were calculated from their paper, while the densities necessary for calculation of molar volume were estimated from various sources. An exceptional article by Bingham and Stookey (5) presents equations for temperature dependence of viscosity of n-alkanes, n-alkyl bromides, and n-alkanethiols. Densities necessary for the calculation of molar volumes were taken from literature sources too numerous to mention. A third article, by Whitmore (42), gives viscosities of $SiRMe_3$ and $SiREt_3$ compounds at $0^\circ C$, $20^\circ C$, and $60^\circ C$, as well as molar volumes at $20^\circ C$. The three points for each compound did not lie on a straight line when graphed as $\log_{10} \eta$ vs. $1/T$. Activation energies were therefore computed by finding the slopes on both sides of 20° and subtracting $1/3$ the difference from the value calculated using the two lower temperatures. Another set of data taken from literature sources is that of Takatani (37). He lists viscosities and densities for several alkyl orthosilicates and energies of activation for these and related alkoxysiloxanes. His data for n-butyl orthosilicate do not agree well with

my values. For instance, my d^{20} 0.8890 compares with his d^{20} 0.8993; my η^{20} 2.095 compares with his η^{20} 2.055. The purity of his compounds is questionable, since his method of reacting ethyl orthosilicate with an alcohol might not be expected to produce an ester free of ethoxy groups. It is noted that the difference in density and viscosity between his data and mine could be predicted if this were the case. He has calculated his temperature dependent viscosity equations as the two-constant form, whereas my data showed too strong a curvature to permit this. I have not recalculated his data, but suspect that it would exhibit the same curvature as mine. It should be noted that the energies of activation for viscous flow from Takatani's data are averages for 35°C and are temperature independent.

A final literature source of data is that of Hurd (23), who presents work on some methyl siloxanes.

The collected information from these literature sources is presented in Tables XIV to XVIII and in Figs. 9 and 10.

D. Interpretation of viscosities and discussion

Melting points of the orthocarbonates

The smooth curve (Fig. 8) obtained by plotting discontinuities vs. molecular weight should dispel any doubts as to their validity as melting points. The literature melting point of -5.5°C for methyl orthocarbonate ties down the curve adequately.

As was mentioned earlier, solution of simultaneous equations led to two possible melting points for ethyl and n-propyl orthocarbonates. It cannot be definitely stated that the ambiguous solutions mean anything, but the fact that the difference between the melting points listed in

