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Studies on Siloxanes. I. The Specific Volume and Viscosity in Relation to Temperature and Constitution

BY CHARLES B. HURD[1]

Introduction

The preparation of pure samples of a number of the simpler siloxanes, including ring compounds and open chain compounds, has made possible the determination of some of their physical properties. The present paper describes methods used to determine specific volumes and viscosities of eleven compounds, as functions of temperature. In addition to presenting the data, this paper includes a discussion of the relations between specific and molar volumes and the temperature and chemical composition. Relations between viscosity and temperature, viscosity and chemical composition, and viscosity and volume are also discussed.

Materials

The compounds used in this work have been described.[2]

As these compounds have long names, a system of abbreviation, already in use, has been employed. This is shown in Table I, which includes the number assigned to the compound on the graphs, the abbreviated formula expressed on the standard functional basis, and the name of the compound.

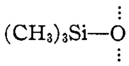
TABLE I

ABBREVIATIONS OF NAMES OF SILOXANES USED

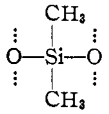
No. on graphs	Code name	Name of compound
1	MM	Hexamethyldisiloxane
2	MDM	Octamethyltrisiloxane
3	MD_2M	Decamethyltetrasiloxane
4	MD_3M	Dodecamethylpentasiloxane
5	MD_4M	Tetradecamethylhexasiloxane
6	D_4	Octamethylcyclotetrasiloxane
7	D_5	Decamethylcyclopentasiloxane
8	D_6	Dodecamethylcyclohexasiloxane
9	D_7	Tetradecamethylcycloheptasiloxane
10	MD*M	Hexamethyl-3,3-diphenyltrisiloxane
11	TM_3	Methyltri-(trimethylsiloxy)-silane

Another name for the last compound is heptamethyl-3-trimethylsiloxytrisiloxane. Its structure is shown later in this paper.

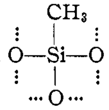
An explanation of the units used in the abbreviated formulas is given, remembering that half of each attached oxygen is included in each unit

M, the monofunctional unit 

$$(\mathrm{CH_3})_3\mathrm{Si}-\overset{\vdots}{\underset{\vdots}{\mathrm{O}}}$$

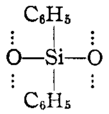
D, the difunctional unit 

$$\overset{\vdots}{\underset{\vdots}{\mathrm{O}}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\overset{\vdots}{\underset{\vdots}{\mathrm{O}}}$$

T, the trifunctional unit 

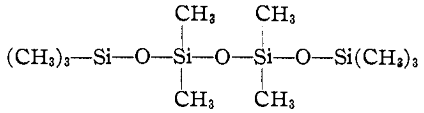
$$\overset{\vdots}{\underset{\vdots}{\mathrm{O}}}-\overset{\mathrm{CH_3}}{\underset{\cdots\mathrm{O}\cdots}{\mathrm{Si}}}-\overset{\vdots}{\underset{\vdots}{\mathrm{O}}}$$

D*, the difunctional unit including $2C_6H_5$ radicals



$$\overset{\vdots}{\underset{\vdots}{\mathrm{O}}}-\overset{\mathrm{C_6H_5}}{\underset{\mathrm{C_6H_5}}{\mathrm{Si}}}-\overset{\vdots}{\underset{\vdots}{\mathrm{O}}}$$

Thus, decamethyltetrasiloxane



$$(\mathrm{CH_3})_3-\mathrm{Si}-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\mathrm{Si}(\mathrm{CH_3})_3$$

is written MDDM or MD_2M.

Specific and Molar Volumes

The specific volumes were determined by measuring the volumes of weighed samples in a dilatometer. This is a standard method. An oil-filled, electrically controlled thermostat was used. Maximum fluctuations in the bath were: 20.00 ± 0.01, 40.00 ± 0.02; 60.00 ± 0.03 and 80.00 ± 0.03°. These fluctuations caused no measurable variation in the volume. The temperature was read on a calibrated Faichney thermometer to 0.01° by a magnifier.

The dilatometers were made by joining a 1.0 ml. graduated pipet to a cylindrical bulb with a capacity of about 5 ml. The volume could be read to an accuracy of ±0.001 ml.

Standard methods of weighing the sample, calibrating the dilatometers with mercury and making stem corrections were used. Apparatus containing siloxanes must be cleaned carefully with alcoholic potash.

The maximum possible error in density and specific volume was 3 parts in 10,000 at room temperature and 4 parts in 10,000 at 60°. Results on distilled water were within this error.

Measurements of the volumes were made at a number of temperatures for each filling, followed by check determinations. No loss of weight occurred except with the most volatile liquid, MM.

Results gave curves which were not quite linear. Values taken from these gave the data for Table II, at intervals of 20°. Table II also gives the values of coefficients a and b in the formula

$$V = V_0(1 + at + bt^2)$$

where t is the centigrade temperature.

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[1] Address: Chemical Laboratory, Union College, Schenectady 8, N. Y.

[2] Patnode and Wilcock, THIS JOURNAL, **68**, 358 (1946).

TABLE II

SPECIFIC VOLUMES AND COEFFICIENTS OF THERMAL EXPANSION OF SOME SILOXANES

No.	Code name	Specific volumes 0°	20°	40°	60°	80°	$a \times 10^3$	$b \times 10^6$
1	MM	1.2800	1.3096	1.3435			1.090	4.50
2	MDM	1.1897	1.2197	1.2510	1.2842	1.3192	1.210	1.90
3	MD_2M	1.1446	1.1715	1.1998	1.2293	1.2602	1.149	1.40
4	MD_3M	1.1173	1.1422	1.1682	1.1955	1.2240	1.087	1.32
5	MD_4M	1.0984	1.1223	1.1473	1.1734	1.2008	1.063	1.26
6	D_4	1.0209	1.0459	1.0720	1.0992	1.1275	1.200	1.35
7	D_5	1.0175	1.0417	1.0664	1.0916	1.1172	1.178	0.60
8	D_6	1.0115	1.0337	1.0563	1.0794	1.1028	1.087	.52
9	D_7	1.0079	1.0281	1.0490	1.0706	1.0930	0.985	.88
10	MD*M	1.0106	1.0279	1.0459	1.0645	1.0838	0.84	.82
11	TM_3	1.1502	1.1769	1.2050	1.2343	1.2652	1.130	1.50

The values for MM are not too dependable, due to a little loss in weight at higher temperatures. Since the specific volumes were taken from curves, the accuracy should be, for example, 1.2090 ± 0.0001.

Table II shows a regular decrease in specific volume, at a given temperature, for both ring and chain compounds as the molecule becomes more complex. This is shown in Fig. 1, where the specific volumes at 20° are plotted against the number of silicon atoms in a molecule.

From Fig. 1 it is evident that the decrease in specific volume is greater for chain compounds than for ring compounds, for each increase of one D group ($(CH_3)_2Si$-O-) in the molecule. The specific volume of a chain compound is greater than that of a ring compound containing the same number of silicon atoms. The chain contains two more methyl groups and one less oxygen than the ring. The ring is more compact, with stronger forces compressing it. Thus, the three membered ring is solid at 20°.

As the molecules become larger, there is less difference between specific volumes of corresponding rings and chains. Probably future work will show little difference between specific volumes of high membered rings and chains, with the same number of Si atoms.

The isomers MD_2M and TM_3, the first a straight chain, the latter a forked chain, show little difference in specific volume, 0.5% higher for the forked chain. Their structural formulas are

MD_2M $(CH_3)_3Si—O—Si(CH_3)_2—O—Si(CH_3)_2—O—Si(CH_3)_3$ $V_{20} = 1.1715$

TM_3 $CH_3—Si[O—Si(CH_3)_3]_3$ $V_{20} = 1.1769$

The molar volumes of these compounds are given in Table III, also the differences $\Delta(MV_{20})$.

TABLE III

MOLAR VOLUMES OF THE SILOXANES

No.	Code	MV_{20}	$\Delta(MV_{20})$
1	MM	212.5	75.8
2	MDM	288.3	75.4
3	MD_2M	363.7	75.6
4	MD_3M	439.3	75.5
5	MD_4M	514.8	
6	D_4	310.0	76.0
7	D_5	386.0	73.6
8	D_6	459.6	73.7
9	D_7	533.3	
10	MD*M	370.5	
11	TM_3	365.4	

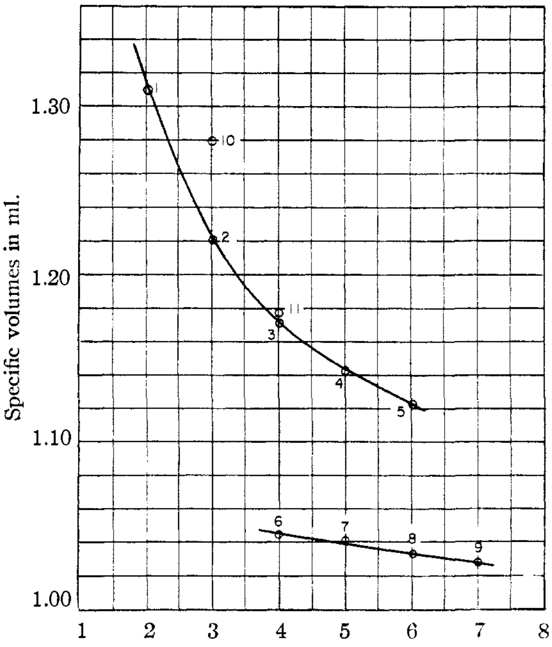

Fig. 1.—Specific volumes of the siloxanes at 20° as a function of number of Si atoms in the molecule.

The differences of MV_{20}, omitting the data for compound MM, which is unsatisfactory due to evaporation, gives an average of MV_{20} = 75.5 per D unit.

By subtracting from MV_{20} for the chains, the product of MV_{20} = 75.5 by the number one less than the silicon atoms in the chain, we have a value of MV_{20} for 1 CH_3 group and 1 $[Si(CH_3)_3]$ unit. This value is $MV_{20}[CH_3—] + MV_{20}[—Si(CH_3)_3]$ = 137.3, 137.2, 137.3 and 137.3, average 137.3.

The rings are composed simply of D units in a ring but, as Kopp[3] and others have found in their investigations of the molar volumes of liquids, the ring structure itself accounts for a certain volume. By subtracting $n \times 75.5$ from MV_{20} for each compound, we have the values given in Table IV.

TABLE IV

MOLAR VOLUME CONTRIBUTED BY RING STRUCTURE

Four membered ring MV_{20}	$= 310.0 - 4(75.5) = 8.0$
Five membered ring MV_{20}	$= 386.0 - 5(75.5) = 8.5$
Six membered ring MV_{20}	$= 459.6 - 6(75.5) = 6.6$
Seven membered ring MV_{20}	$= 533.3 - 7(75.5) = 4.8$

When data on specific volumes of other liquid compounds containing Si, O and CH_3 groups are available, we may calculate individual values for MV_{20} for Si, O, C and H.

Table V gives formulas for calculating the molar volumes, MV_{20}, for siloxanes containing n Si atoms per molecule.

TABLE V

FORMULAE FOR CALCULATING MOLAR VOLUMES OF SOME SILOXANES

Straight chain	$MV_{20} = 137.3 + (n-1)75.5$	Very satisfactory
Forked chain	$MV_{20} = 139.0 + (n-1)75.5$	
Ring, 4 or 5 member	$MV_{20} = 8.3 + n \times 75.5$	
Ring, 6 member	$MV_{20} = 6.6 + 6 \times 75.5$	
Ring, 7 member	$MV_{20} = 4.8 + 7 \times 75.5$	
Ring, 10 or more member	$MV_{20} = 2 + n \times 75.5$	Estimated

Viscosities

The viscosities of the eleven siloxanes have been determined by the method of Bingham.[4] Two viscosity pipets were used to cover the eleven liquids. They were calibrated by standard liquids from the Bureau of Standards and were checked against each other on MD_2M.

The formula used was

$$\eta = Cpt - C'p/t \tag{1}$$

The constants for the pipets and the liquids measured were: Pipet V-2; $C = 4.363 \times 10^{-6}$, $C' = 2.09$ used for liquids D_4, D_5, D_6, D_7, MD_2M, MD_3M, MD_4M, MD^*M, TM_3; Pipet V-80; $C = 9.010 \times 10^{-6}$, $C' = 1.43$ used for liquids MM, MDM, MD_2M.

In determinations of the viscosity, the arrangement of stopcocks permitted pressure to be applied to the left side of the pipet for a run "down" through the capillary or to the right side for a run "up." Check runs were made in this way for each liquid at each temperature. The pressure was supplied from a large tank of air and was read as hydrostatic pressure on a metal scale. The electrically controlled thermostat, already described, was used, also an electrical timer. Since the thermostat vessel was an unsilvered Dewar flask, the flow of liquid through the viscometer was easily observed.

The data were plotted in two ways, first the viscosity against temperature and, second, the logarithm of the viscosity against reciprocal absolute temperature, each on large coördinate

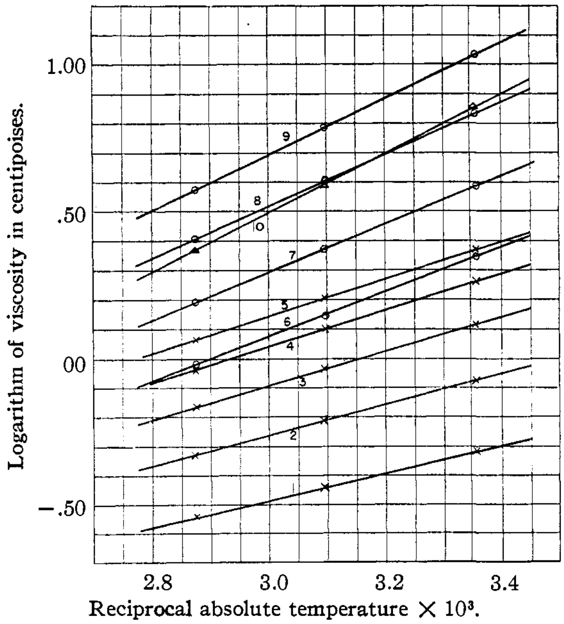

Fig. 2.—Logarithms of viscosities of the siloxanes as functions of the reciprocal absolute temperature.

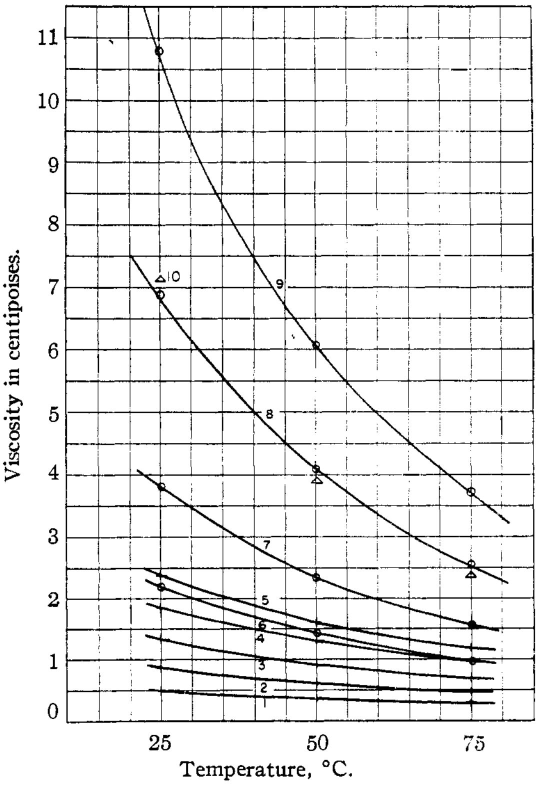

Fig. 3.—Viscosities of the siloxanes as functions of temperature.

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[3] Kopp, *Pogg. Ann.*, **47**, 113 (1839), through *Ann.*, **250**, 1 (1889).

[4] Bingham, "Fluidity and Plasticity," 1st ed., McGraw-Hill Book Co., New York, N. Y., 1922, Chap. V, Fig. 29, p. 76.

TABLE VI

VISCOSITIES OF THE SILOXANES, WITH THE CONSTANTS FOR EQUATION 3 AND BATSCHINSKI'S EQUATION

No.	Code	Viscosities in centipoises 25°	50°	75°	$Q\eta$, calories	A	C	ω
1	MM	0.4881	0.3661	0.2874	2166	−1.903	0.0789	1.1443
2	MDM	0.8463	.6144	.4705	2446	−1.867	.0880	1.1233
3	MD$_2$M	1.310	.9280	.6910	2670	−1.842	.1081	1.0959
4	MD$_3$M	1.826	1.266	.9301	2782	−1.781	.1301	1.0772
5	MD$_4$M	2.372	1.609	1.168	2892	−1.750	.1507	1.0649
6	D$_4$	2.200	1.405	0.961	3417	−2.162	.1162	.9996
7	D$_5$	3.824	2.358	1.562	3714	−2.141	.1656	1.0051
8	D$_6$	6.875	4.060	2.544	4099	−2.170	.2279	1.0055
9	D$_7$	10.775	6.060	3.716	4369	−2.175	.3088	1.0041
10	MD*M	7.120	3.895	2.363	4553	−2.490	.1642	1.0093
11	TM$_3$	1.360	0.9517	0.7055	2702	−1.850	.1082	1.1041

paper. The second type curves were absolutely linear, within experimental error. From these second, linear curves, points were taken for 25.00, 50.00 and 75.00°, giving the data for Fig. 2 and Table VI, also for Fig. 3. The compounds are indicated by number in Table I.

The linear relation between log η and $1/T$, shown by Fig. 2, indicates that the siloxanes are normal liquids over the range studied, 20 to 80°. It may be expressed by the equation[5]

$$\log \eta = B/T + A \qquad (2)$$

or more recently by the equation

$$\log \eta = Q\eta/2.30\,RT + A \qquad (3)$$

where $Q\eta$ is called the energy of activation of viscous flow.[6] This $Q\eta$ is 2.30 R times the slope of the lines of Fig. 2, for logarithm of viscosity against reciprocal absolute temperature. In Table VI are given the viscosities, together with values of $Q\eta$ and A of equation (3) and constants C and ω of Batschinski's equation.

The relation between $Q\eta$, the energy of activation for viscous flow, and $\Delta H_{\text{vap.}}$, the molar heat of vaporization, has been noted for a number of liquids. Although ΔH has not been measured for these siloxanes, we may estimate it by Trouton's rule, assuming these siloxanes are normal liquids.

$$\Delta H_{\text{vap.}} = 20.5\ T_{\text{B.p.}} \qquad (4)$$

Since some attention has been paid to the relation between $Q\eta$ and $\Delta\epsilon_{\text{vap.}}$, we may estimate $\Delta\epsilon_{\text{vap.}}$ by formula (5).

$$\Delta\epsilon_{\text{vap.}} = \Delta H_{\text{vap.}} - RT \qquad (5)$$

This formula assumes a perfect gas but is a good approximation.

In Table VII are given the values of $\Delta H_{\text{vap.}}$ and $\Delta\epsilon_{\text{vap.}}$, as well as the ratios. No data are given for MD*M nor for MD$_4$M, their boiling points being uncertain.

The data of Table VII show that $Q\eta/\Delta H_{\text{vap.}}$ is considerably higher for ring than chain types of siloxanes. If we accept the theory of holes in liquids to account for viscous flow,[7] we must conclude that it is necessary to open proportionally larger holes for flow of ring compounds than for chain compounds. In view of their structure, this conclusion is reasonable.

TABLE VII

RELATION BETWEEN $Q\eta$ AND $\Delta H_{\text{vap.}}$ AND $\Delta\epsilon_{\text{vap.}}$

No.	Code	B. p., °C.	$\Delta H_{\text{vap.}}$	$\frac{Q\eta}{\Delta H_{\text{vap.}}}$	$\frac{Q\eta}{\Delta\epsilon_{\text{vap.}}}$
1	MM	373	7647	0.284	0.314
2	MDM	426	8733	.280	.310
3	MD$_2$M	467	9573	.280	.309
4	MD$_3$M	502	10291	.271	.300
6	D$_4$	448	9184	.371	.412
7	D$_5$	483	9902	.375	.416
8	D$_6$	518	10619	.386	.427
9	D$_7$	553	11337	.385	.426
11	TM$_3$	463	9520	.284	.314

The relation between log η and $Q\eta$ is shown on semi-log coördinates by Fig. 4. At constant temperature, this relation is linear for the four

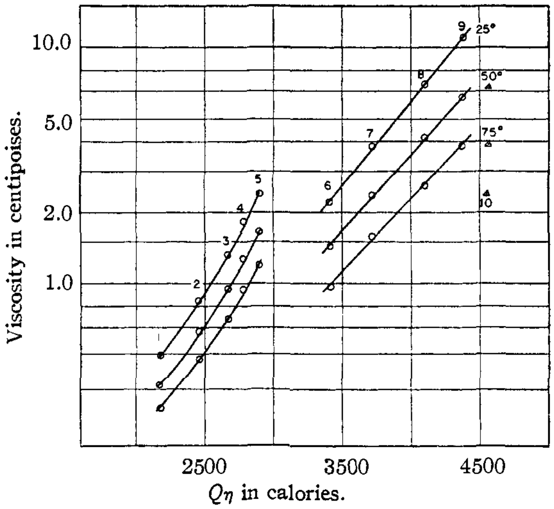

Fig. 4.—Relation between viscosity and $Q\eta$ at three temperatures for the siloxanes.

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[5] Drucker, *Z. physik. Chem.*, **92**, 287 (1918).

[6] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw Hill Book Co., Inc., New York, N. Y., 1941, p. 493.

[7] Powell, Roseveare and Eyring, *Ind. Eng. Chem.*, **33**, 430 (1941).

ring compounds at each of the three temperatures. For the chain compounds, the log η increases a little more rapidly than $Q\eta$ as the chain length increases.

The relation between $Q\eta$ and the number of silicon atoms, n, in the molecule, is shown by Fig. 5. For the ring compounds, the value of $Q\eta$ increases as a linear function of the number of silicon atoms; for the chains it shows less than a linear increase.

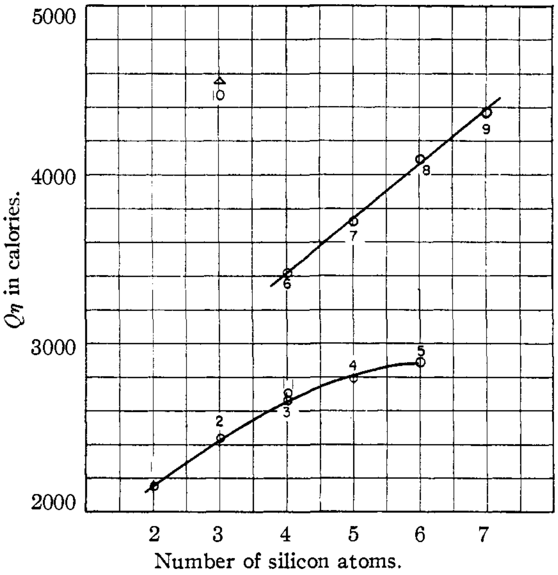

Fig. 5.—Relation between $Q\eta$ and number of silicon atoms in the siloxane molecule.

Thus, the chain compounds show less increase in $Q\eta$ than would be expected as chain length increases. The same effect has been shown for petroleum hydrocarbons.

The relation between log η and log n is approximately linear for the chains and shows only slight curvature for the rings. This is shown by Fig. 6. These curves may be used for extrapolation to higher values of n, within reason. Extrapolation to lower values would appear to give intersection of the two curves for $n = 2$. However, the three-membered ring is solid at 25°; the two-membered ring would also probably be solid, if it existed.

The two isomers, MD_2M and TM_3, give an interesting comparison. Their formulas are

MD_2M $(CH_3)_3Si—O—Si(CH_3)_2—O—Si(CH_3)_2—O—Si(CH_3)_3$

TM_3 $CH_3—Si[O—Si(CH_3)_3]_3$

They have nearly the same boiling points (467 and 463°, Table VII), very nearly the same viscosity (1.310 and 1.360 at 25°, Table VI), and their $Q\eta$ values are 2670 and 2702, Table VI. Their A values are -1.842 and -1.850, Table VI. Although TM_3 is a shorter, thicker molecule than the straight chain MD_2M and might thus be expected to differ considerably, such is not the case.

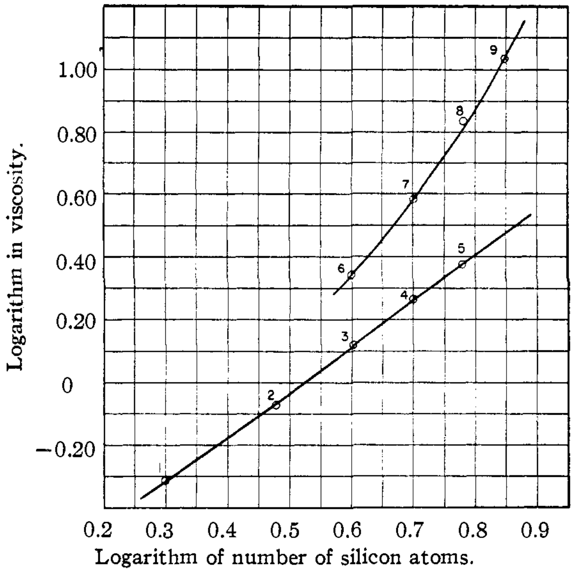

Fig. 6.—Relation between logarithm of viscosity of the siloxanes and logarithm of the number of silicon atoms in the molecule.

The significance of the value A in equation 3 and Table VI is not entirely clear. The value of A for octane in the literature,[8] when reduced to comparative units, falls between the values for D_7 and MD_4M.

The values for A in Table VI fall between -2.141 and -2.175 for the rings, a nearly constant value. For the chains the value of A increases, with increasing complexity of the compound from -1.903 for MM to -1.750 for MD_4M. Values for isomers MD_2M and TM_3 are -1.842 and -1.850. The values of A for chains are larger, less negative, than for rings. The diphenyl compound, MD*M, has a much more negative value, $A = -2.490$, than the value for the corresponding all methyl compound, MDM, where $A = -1.867$.

Ward[9] claims that $Q\eta$ changes with change of temperature for liquids whose coördination or type of association changes with temperature. The data of this paper show no change in $Q\eta$ over the interval studied, 20 to 80°. Thus, the molecular complexity of these siloxanes appears to change little, if at all, over this range.

Relations between Viscosity and Specific or Molar Volumes

Of the equations showing a relation between viscosity and specific volume, probably the best known is that of Batschinski,[10] usually written

$$\eta = C/(V - \omega) \qquad (6)$$

where η is the viscosity, C and ω are constants and V the specific volume. The term ω is spoken of as

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[8] "Second Report on Viscosity and Plasticity," Nordemann Publishing Co., Inc., New York, N. Y., 1938, p. 69.

[9] Ward, *Trans. Faraday Soc.*, **33**, 92 (1937).

[10] Batschinski, *Z. physik. Chem.*, **84**, 643 (1913).

a fixed volume, intermediate between that of the solid, V_s and the liquid, V. The difference, $V - \omega$, is thought of as the free space within the liquid which permits motion of the liquid molecules during viscous flow.[11] This equation has been shown to give excellent results with many liquids, especially where $V - \omega$ is 0.1 or larger.[12]

From data given in Table II for specific volumes and in Table VI for viscosities for the three temperatures, 25, 50 and 75°, the values of C and ω were calculated. These data are also tabulated in Table VI.

These values of C, in Batschinski's equation, show a nearly linear relation to n, the number of silicon atoms in a molecule, as is evident in Fig. 7. For the same value of n, C is larger for ring than chain compounds. The curves appear to meet where $n = 3$.

From Table VI it is evident that values of ω decrease for the chains, as n increases in a nearly linear relation. For the rings, ω is nearly constant.

Batschinski found the product of the molecular weight by ω showed regular additive properties. Using the values for all of the chains except MM, whose vaporization made the value for the specific volume inaccurate, we find the values for Table VIII.

TABLE VIII

THE MOLAR FIXED VOLUME, $M\omega$, FOR THE CHAIN TYPE SILOXANES

Compound	M	ω	$M\omega$	$\Delta(M\omega)$
MDM	236.37	1.1233	265.5	74.7
MD_2M	310.48	1.0959	340.2	74.1
MD_3M	384.59	1.0772	414.3	74.0
MD_4M	458.70	1.0649	488.3	

If we use the average of the three values for $\Delta(M\omega)$, which is actually the value for the group $Si(CH_3)_2$-O-, and use Batschinski's equation

$$M\omega = \Sigma n\epsilon \qquad (7)$$

where ϵ is a constant for each atom and is additive to give the value of $M\omega$ and use, also, Batschinski's values $\epsilon_H = 4.3$, $\epsilon_C = 8.8$ and $\epsilon_O = 8.6$, we find

$$\epsilon_{Si} = 74.30 - 6\epsilon_H - 2\epsilon_C - \epsilon_O = 22.3$$

Using this constant for ϵ_{Si}, we obtain, by addition, $M\omega$ for the compound MD_2M to be 332.1, within 2% of the value of 340.2 in Table VIII. Thus, our atomic constant $\epsilon_{Si} = 22.3$ may take its place with Batschinski's constants.

Bingham[13,14] has described a quantity which he has called the "atomic temperature constant of fluidity." He states that the constant for each element, multiplied by the number of atoms of that element in the molecule gives a number for each element in the compound. The sum of these numbers gives the temperature at which the compound attains a certain fluidity. Bingham and Spooner[14] have tabulated these constants for several elements for seven fluidities, ranging from 10 to 500 reciprocal poises. They gave no value for silicon.

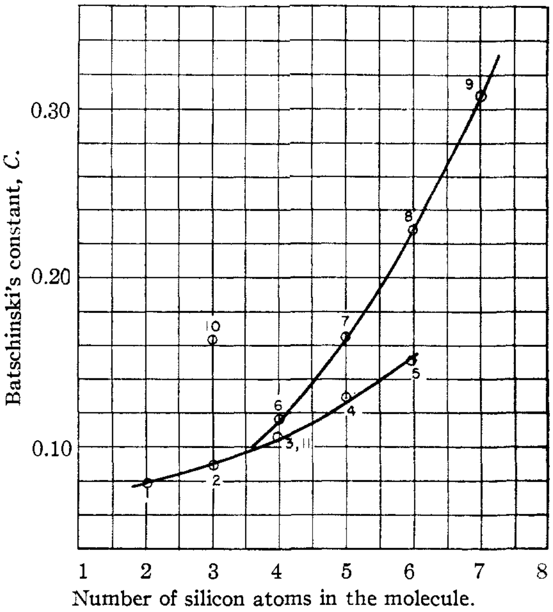

Fig. 7.—Relation between Batschinski's constant C and the number of silicon atoms in the molecule.

Using Bingham and Spooner's values, we may attempt to find ϵ_{Si}. One should note that this is not the value ϵ_{Si} for Batschinski's $M\omega$.

MDM $\varphi = 100$ $T = 286.6$°K. gives $\epsilon_{Si} = -95.7$

MD_2M $\varphi = 100$ $T = 317.2$°K. gives $\epsilon_{Si} = -101.7$.

These figures compare with Bingham and Spooner's $\epsilon_C = -82.9$ for $\varphi = 100$. The value for silicon is thus reasonable.

Bingham has shown how to estimate the degree of association in the liquid. Using his formula, we find an indication of about 30% association in these chain siloxanes. This information is not exact but may be taken as an indication.

Summary

Specific volumes and viscosities of eleven siloxanes have been measured. Four of the compounds were ring type and seven were chain type. Ten contained only methyl groups, one contained two phenyl and six methyl groups.

Coefficients for the equation $V = V_0(1 + at + bt^2)$ are tabulated. Specific volumes increase with rising temperature, decrease with increasing number of silicon atoms in ring or chain. Specific volumes of chain compounds are larger than those of corresponding rings, but approach the latter as the number of Si atoms is increased.

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(11) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," 1st ed., McGraw-Hill, Inc., New York, N. Y., 1941, p. 487.

(12) "Second Report on Viscosity and Plasticity," Nordemann Pub. Co., Inc., New York, N. Y., 1938, p. 47.

(13) Bingham, "Fluidity and Plasticity," 1st ed., McGraw Hill Book Co., New York, N. Y., 1922, pp. 113–126.

(14) Bingham and Spooner, *J. Rheology*, **3**, 221 (1932).

Molar volumes, MV_{20}, were calculated for the compounds, also for groups $Si(CH_3)_2$-O-, for $[CH_3 + Si(CH_3)_3]$ and for the contribution from the ring structure.

Graphs for the relation of log η and reciprocal T°K. show a linear relation. Values for $Q\eta$ and A in formula $\log \eta = Q\eta/2.30\,RT + A$ are tabulated.

The ratios of $Q\eta$ to ΔH and $\Delta\epsilon$ of vaporization are given.

The relation between η and n, also between $Q\eta$ and n, are given by graphs.

A curve is given to permit estimation of viscosities of more complex, pure siloxanes than have been prepared.

Values of η, $Q\eta$ and A are nearly the same for two isomers, a straight chain and a branched chain, in spite of the different structure.

Using Batschinski's equation, $\eta = C/(V - \omega)$, values of C and ω were calculated, also a value $\epsilon_{Si} = 22.3$ for Batschinski's additive relation $M\omega = \Sigma n\epsilon$.

There is slight evidence of some association in these liquids.

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[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

High-Temperature Heat Contents of Titanium Carbide and Titanium Nitride[1]

BY B. F. NAYLOR[2]

Two recent publications[3] of the Pacific Experiment Station of the Bureau of Mines have presented some thermodynamic data for a few metallurgically important compounds of titanium. In continuation of this program of study, the present paper reports high-temperature heat-content measurements for titanium nitride and titanium carbide, two of the products resulting from the addition of titanium to steel and alloys. No previous similar data exist for either of these substances.

Method and Materials

The heat content measurements were made by the "drop" method. The experimental procedure and apparatus have been described previously.[4] The copper calorimeter was calibrated with electrical energy, measured in international joules, and the results were converted to the conventional calorie by the relation,[5] 1 cal. = 4.1833 int. joules (NBS).

During the measurements the samples were enclosed in platinum-rhodium alloy capsules, the heat contents of which were determined separately. The capsules, after being filled with sample, were evacuated of air, filled with helium, and then quickly sealed.

Titanium carbide was prepared by heating powdered metallic titanium with Norblack (99.7% carbon) *in vacuo* at 1,300-1,350°. After grinding to −150 mesh and analyzing, the titanium to carbon ratio was adjusted by adding whichever element was deficient, and then the sample was reheated under similar conditions. Analysis of the final product gave 79.56% titanium and 19.85% carbon and it was calculated to be 99.0% titanium carbide. The principal impurity was about 0.4% unreacted titanium. The analytical results were confirmed by determinations kindly made for us by the Titanium Alloy Manufacturing Co.

Titanium nitride was made by heating powdered titanium in a stream of purified nitrogen and hydrogen, first at 1,000° and finally for ten hours at 1,400°. The product, which was bronze colored, analyzed 77.04% titanium, corresponding to 99.6% titanium nitride content. Silicon nitride probably was the chief impurity.

Results

Fifteen experimental heat content determinations of titanium carbide and fourteen of titanium nitride were made. The results are listed in Table I and also are shown graphically in Fig. 1. In Table I the column labeled T, °K., gives the temperature of the sample immediately before dropping into the calorimeter and $H_T - H_{298.16}$ represents the heat liberated per gram molecular weight in cooling to 298.16°K. The molecular weights accord with the 1941 International Atomic Weights and the sample weights were corrected to vacuum, using the experimentally determined densities, titanium carbide = 4.81 and titanium nitride = 5.24 g./cc.

TABLE I

HEAT CONTENTS ABOVE 298.16°K.

TiC (mol. wt. = 59.910)		TiN (mol. wt. = 61.908)	
T, °K.	$H_T - H_{298.16}$ (cal./mole)	T, °K.	$H_T - H_{298.16}$ (cal./mole)
360.5	576	388.3	875
450.9	1,459	410.6	1,122
587.8	2,943	499.7	2,085
671.5	3,905	615.4	3,407
790.5	5,270	687.3	4,250
891.5	6,470	807.5	5,690
1001.7	7,860	931.7	7,200
1103.0	9,080	1010.0	8,160
1205.1	10,400	1123.3	9,620
1288.2	11,450	1203.5	10,670
1391	12,770	1312	12,080
1454	13,570	1435	13,690
1537	14,600	1559	15,320
1674	16,340	1738	17,760
1735	17,120		

The values for titanium carbide given in Table I include a small correction of less than 0.1% for

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[2] Formerly chemist, Pacific Experiment Station, Bureau of Mines.

[3] (a) K. K. Kelley, *Ind. Eng. Chem.*, **36**, 865 (1944); (b) B. F. Naylor, THIS JOURNAL, **67**, 2120 (1945).

[4] J. C. Southard, *ibid.*, **63**, 3142 (1941).

[5] E. F. Mueller and F. D. Rossini, *Am. J. Phys.*, **12**, 1–7 (1944).