tropy are different from those functions for the liquid has been fitted to isotherms in the range of relative pressures of 0.05 to 0.98. For porous solids equations have been presented for adsorption on solids in which the area available to each succeeding layer is less than the previous one. A new-type equation has been developed for adsorptions limited to n-layers which has better properties than the n-equation of B. E. T.[3]

PITTSBURGH, PA. RECEIVED DECEMBER 29, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Vapor Pressure–Viscosity Relations in Methylpolysiloxanes

BY DONALD F. WILCOCK

Liquid methylpolysiloxane mixtures, or silicone oils, exhibit unusually small changes in viscosity with temperature. Their viscosities at 100°F. are only about two and one-half times those at 210°F., while the corresponding factor for a petroleum oil of viscosity index 100 is about eight. This behavior of silicone oils suggested investigation of the relations between the viscous properties and the vapor pressure–temperature characteristics of those smaller polysiloxane molecules which may be separable as pure compounds.

The viscosities at several temperatures of a number of the linear and cyclic methylpolysiloxanes have been reported by Hurd,[1] and these same compounds were available for determination of vapor pressures. In addition the eight-silicon ring, hexadecamethylcyclooöctasiloxane,[2] and the seven- to eleven-silicon chain compounds, hexadecamethylheptasiloxane to tetracosamethylundecasiloxane, were isolated and their vapor pressures, viscosities and densities were determined. Analysis of these data has yielded general equations relating vapor pressure to temperature and to the number of silicon-containing units. Similar equations relating viscosity to temperature and to the number of units have also been obtained. Estimates of the average size of the segmental unit of flow in the large polymeric chains likewise have been made by comparison of the viscous and vapor pressure properties.

For the sake of clarity and conciseness, the proper names of the methylpolysiloxane compounds will be abbreviated by use of a shorthand system of nomenclature based on the functionality of the basic silicon-containing units which appear in the molecules. The bifunctional repetitive unit, $(CH_3)_2SiO$, is termed a **D**-unit, and the monofunctional terminal group, $(CH_3)_3SiO_{1/2}$, is termed an **M**-unit. Using this system, simple cyclic molecules are written $\mathbf{D}_x$, and linear molecules are written $\mathbf{M}_2\mathbf{D}_{x-2}$, x being the total number of silicon containing units.

Experimental

The cyclic compound $\mathbf{D}_8$ was isolated by Patnode[3] by fractional distillation of the hydrolyzate of dimethyldichlorosilane. The linear compounds $\mathbf{M}_2\mathbf{D}_5$ to $\mathbf{M}_2\mathbf{D}_9$ were isolated by fractionally distilling through a packed column at reduced pressure the volatile portions from equilibrated[4] silicone oils. The fractions were carefully redistilled, but it was not possible to eliminate completely small amounts of the corresponding cyclic compounds which were present, because at distillation temperatures near 200° the boiling points of the cyclic compounds approach those of the corresponding linear compounds as the number of units is increased (see Fig. 2) The method of specific refraction[5] was used to determine the percentage of cyclic methylpolysiloxanes present as impurity, with the results shown in Table I. The compound $\mathbf{M}_2\mathbf{D}_5$ was not redistilled, and consequently was less pure than the others.

TABLE I

ANALYSIS OF NEW LINEAR METHYLPOLYSILOXANES

Compound	Density 20°	Refractive index at 20°	Specific ref.	Me: Si ratio	Wt. % chain
$\mathbf{M}_2\mathbf{D}_5$	0.911	1.3965	0.2640	2.234	82
$\mathbf{M}_2\mathbf{D}_6$	.913	1.3970	.2638	2.230	92
$\mathbf{M}_2\mathbf{D}_7$	.918	1.3980	.2629	2.212	96
$\mathbf{M}_2\mathbf{D}_8$	.925	1.3988	.2615	2.186	93
$\mathbf{M}_2\mathbf{D}_9$	.930	1.3994	.2604	2.165	91

Vapor pressures were determined by noting the boiling point of each compound at several pressures. A 14″ × 1/2″ jacketed distillation column packed with 3/32″ stainless steel helices was fitted just above the reflux condenser with a side tube connection leading to a McLeod gage capable of reading pressures as high as 50 mm. Pressure at the head of the column was regulated with a manostat capable of holding pressure within 0.1 mm. Pressures above 50 mm. were read from a manometer. Each compound was placed in the still pot and slowly distilled at constant pressure until the vapor temperature at total reflux was within 0.1° of the temperature during partial takeoff. The temperature was then noted and the process repeated at other pressures. The experimental values are summarized in Table II.

Kinematic viscosities were determined in modified Ostwald pipet viscometers at 100 ± 0.1°F. and 210 ± 0.1° F., with a precision of 0.5%. Absolute viscosities were calculated from the kinematic values and the densities. Densities were determined in a 4.5 cc. dilatometer at 20 ± 0.1° with a precision of 0.05%. Refractive indices were measured with an Abbe-type refractometer at 20 ± 0.1° using the sodium D-line.

Vapor Pressures

The vapor pressure–temperature curves for both the cyclic and linear series of compounds are plotted in Fig. 1. These log p *vs.* $1/T$ curves are straight lines for both the linear and cyclic com-

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[1] Charles B. Hurd, THIS JOURNAL, 68, 364 (1946).

[2] For a discussion of organosilicon nomenclature, see R. O. Sauer, *J. Chem. Ed.*, 21, 303 (1944).

[3] Winton Patnode and D. F. Wilcock, THIS JOURNAL, 68, 358 (1946).

[4] The process of equilibration, see ref. 3, involves an equilibrium rearrangement of the **M** and **D** units into a system comprising linear polysiloxanes using sulfuric acid as a catalyst.

[5] Sauer, THIS JOURNAL, in press.

TABLE II

BOILING POINTS OF METHYLPOLYSILOXANES

Compound	Press., mm. Hg	B. p., °C.	$(1/T) \times 10^3$
D_4	758	175.8	2.228
	20	73.4	2.886
D_5	760	210	2.07
	20	101	2.67
D_6	100	170.0	2.26
	20	128.2	2.49
	4.2	95.2	2.716
D_7	99.5	193.0	2.146
	20	150.7	2.360
	4.8	118.8	2.552
D_8	39.2	192.0	2.150
	4.9	141.6	2.412
	1.9	124.8	2.514
M_2	757	100.1	2.680
	161.5	54.1	3.057
	100	42.7	3.167
M_2D	747	151.7	2.355
	154	99.0	2.688
	40	66.5	2.946
M_2D_2	760	194	2.14
	20	88	2.77
M_2D_3	760	229	1.99
	20	117	2.56
M_2D_4	101	184.2	2.187
	49	165.0	2.283
	20	141.4	2.413
	5.0	112.0	2.597
M_2D_5	40	184.5	2.186
	20	165.2	2.282
	10	149.0	2.370
	3.2	125.9	2.506
M_2D_6	39.3	202.0	2.105
	20.0	185.6	2.180
	5.1	153.3	2.346
	2.7	141.2	2.414
M_2D_7	16.0	198.8	2.120
	4.9	172.5	2.245
	4.05	170.1	2.257
	2.7	160.6	2.306
	0.29	122.2	2.530
M_2D_8	10.0	202.8	2.102
	4.1	182.6	2.195
	2.7	176.1	2.227
	1.1	161.3	2.303
	0.45	146.8	2.382
M_2D_9	4.7	201.8	2.106
	1.1	176.3	2.226
	0.30	153.1	2.347

pounds and have been extrapolated to room temperature. The vapor pressures are plotted in Fig. 2 as a function of the number of units for temperatures of 30, 100 and 200°. The vapor pressure decreases logarithmically in each series with increase in the molecular size.

The latent heat of vaporization, ΔH_{vap}, increases regularly with the molecular size in both the linear and cyclic series. It has been determined for each compound by the Clapeyron–Clausius equation, and is plotted in Fig. 3 as a function of the number of units. The straight lines were fitted by the method of least squares, and their equations are

$$\text{Cyclic: } \Delta H_{\text{vap}} = 5.45 + 1.35x \quad (\text{kcal.}) \tag{1}$$

$$\text{Linear: } \Delta H_{\text{vap}} = 4.70 + 1.65x \quad (\text{kcal.}) \tag{2}$$

where x again refers to the number of units in the molecule. The agreement between the experimental values and those calculated from equations (1) and (2) is shown in Table III. The deviations are less than 4% for the chain compounds and less than 2% for the ring compounds. The increment in ΔH_{vap} per **D**-unit is 300 calories greater in the linear than in the cyclic series of molecules. The linear variation of the molar latent heat of vaporization of the methylpolysiloxanes with the number of silicon atoms per molecule is unexpected in view of the fact that the molar heats of vaporization of the straight chain aliphatic hydrocarbons as reported by Doss[6] are a non-linear function of the number of carbon atoms, and in fact reach a maximum value of 9.56 kcal. for the compound $C_{14}H_{30}$.

TABLE III

LATENT HEATS OF VAPORIZATION

Compound	ΔH_{vap} (kcal. per mole) Experimental	Calcd.	Deviation
D_4	10.9	10.85	−0.05
D_5	12.0	12.2	+ .2
D_6	13.75	13.55	− .2
D_7	14.9	14.9	0
D_8	16.2	16.25	+ .05
M_2	8.3	8.00	− .30
M_2D	9.45	9.65	+ .20
M_2D_2	11.5	11.30	− .20
M_2D_3	12.7	12.95	+ .25
M_2D_4	14.6	14.60	0
M_2D_5	16.25	16.25	0
M_2D_6	17.2	17.9	+ .70
M_2D_7	19.4	19.55	+ .15
M_2D_8	22.0	21.20	− .80
M_2D_9	22.8	22.85	+ .05

The linear dependence of ΔH_{vap} upon the number of silicon atoms per molecule, together with the linear dependence of log p upon the same variable, as shown in Fig. 2, permits the derivation of a useful expression giving the vapor pressure as a function of temperature and composition. The equation

$$\log p_L = 4.10 - 0.318x.\ x \geqslant 5 \tag{3}$$

expresses the relation between log p and x at 200° shown in Fig. 2 for the linear compounds. The integrated form of the Clapeyron–Clausius equation may be written

$$\log p_L = A - \frac{\Delta H_{\text{vap}}}{2.303RT} \tag{4}$$

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[6] M. P. Doss, "Physical Constants of the Principal Hydrocarbons," The Texas Co., New York City, N. Y., 1943.

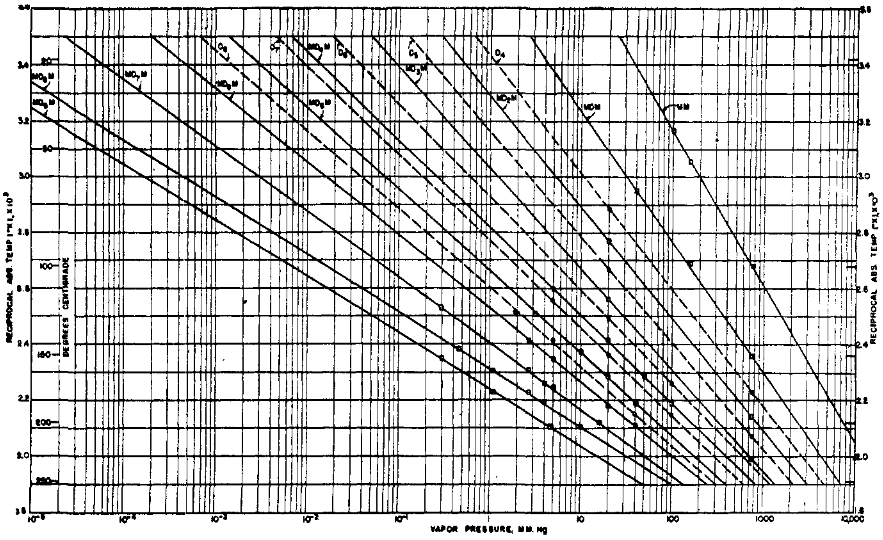

Fig. 1.—Vapor pressures of linear and cyclic methylpolysiloxanes.

Substituting (2) in (4) and rearranging

$$\log p_{\mathrm{L}} = A - \frac{1030}{T} - \frac{360}{T}x \qquad (5)$$

At 200°, this becomes

$$\log p_{\mathrm{L}} = A - 2.18 - 0.761x \qquad (6)$$

Equating (6) and (3)

$$A = 6.28 + 0.443x \qquad (7)$$

Substituting (7) in (5), the general vapor pressure relation for linear methylpolysiloxanes ($x \geqslant 5$) is obtained

$$\log p_{\mathrm{L}} = 6.28 - \frac{1030}{T} + \left[0.443 - \frac{360}{T}\right]x \qquad (8)$$

The general vapor pressure relation for the cyclic methylpolysiloxanes ($x \geqslant 4$) is obtained by a similar procedure.

$$\log p_{\mathrm{R}} = 7.07 - \frac{1190}{T} + \left[0.265 - \frac{294}{T}\right]x \qquad (9)$$

The lines in Fig. 2 for the temperatures 100° and 30° have been drawn using equations (8) and (9)

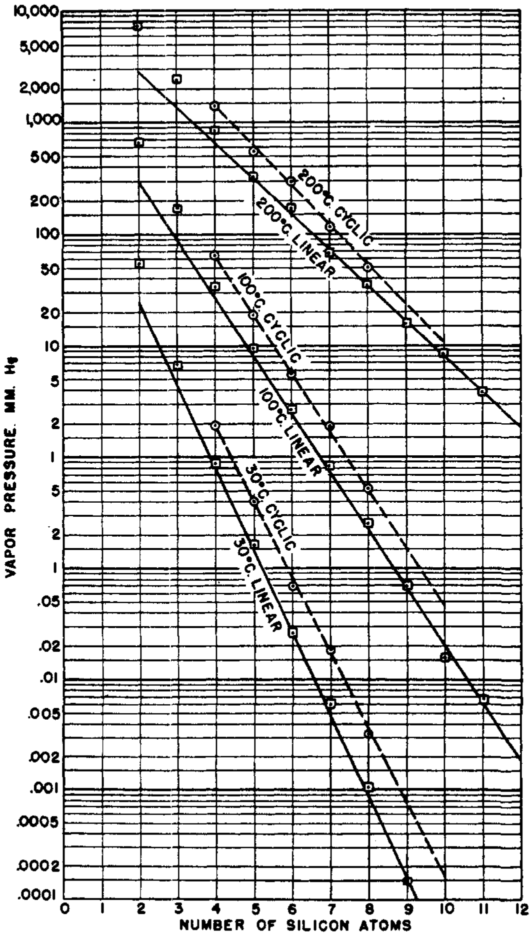

Fig. 2.—Vapor pressure *vs.* composition at constant temp.

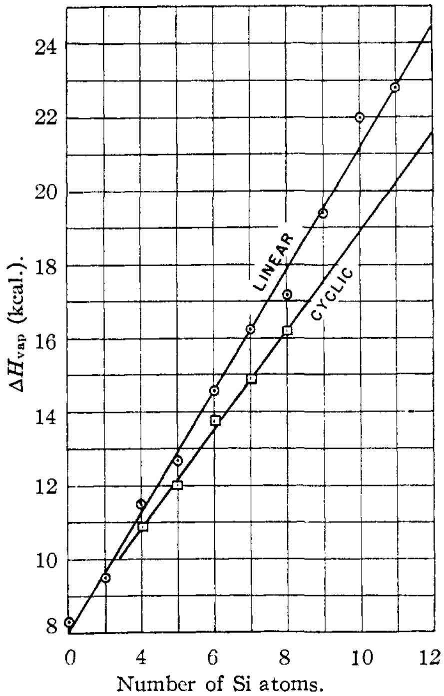

Fig. 3.—Latent heats of vaporization of linear and cyclic methyl polysiloxanes

Viscous Properties

The viscosities of the linear methylpolysiloxanes up to $\mathbf{M_2D_4}$ and of the cyclic compounds up to $\mathbf{D_7}$ have been reported by Hurd.[1] The viscosities of the linear compounds up to $\mathbf{M_2D_9}$ and of the

TABLE IV

VISCOUS PROPERTIES OF LINEAR AND CYCLIC METHYL POLYSILOXANES

Compound	Viscosity in Centipoises 100°F.	210°F.	E_{vis} kcal.	ln η_∞	ln η_∞ (calcd.)
D_4	1.69	0.700	3.42	−4.97	−4.95
D_5	2.94	1.11	3.71	−4.92	−4.96
D_6	5.10	1.75	4.10	−4.99	−4.97
D_7	7.80	2.79	4.37	−5.01	−4.98
D_8	10.7	3.25	4.50	−4.89	−4.98
M_2	0.412	0.236	2.17	−4.49	−4.44
M_2D	0.703	.373	2.45	−4.31	−4.29
M_2D_2	1.09	.541	2.67	−4.22	−4.19
M_2D_3	1.50	.716	2.78	−4.09	−4.11
M_2D_4	1.91	.883	2.89	−4.01	−4.04
M_2D_5	2.58	1.15	3.04	−3.96	−3.98
M_2D_6	2.87	1.26	3.10	−3.96	−3.93
M_2D_7	3.38	1.47	3.13	−3.85	−3.89
M_2D_8	3.94	1.65	3.27	−3.92	−3.85
M_2D_9	4.52	1.89	3.28	−3.80	−3.82

cyclic **D**$_8$ have now been determined, and are reported in Table IV, columns 2 and 3. The viscosities at 100°F. are plotted in Fig. 4 as a function of the number of units. The logarithm of the absolute viscosity is seen to be a linear function of the logarithm of the number of units for each series, the relation being

$$\log \eta_L = -0.82 + 1.41 \log x \qquad (10)$$

for the linear compounds, and

$$\log \eta_R = -1.44 + 2.74 \log x \qquad (11)$$

for the cyclic compounds, at $T = 311$°K.

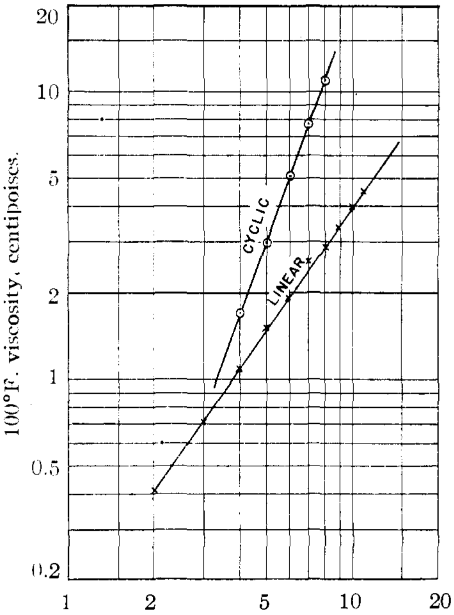

Fig. 4.—Viscosities of linear and cyclic methyl polysiloxanes.

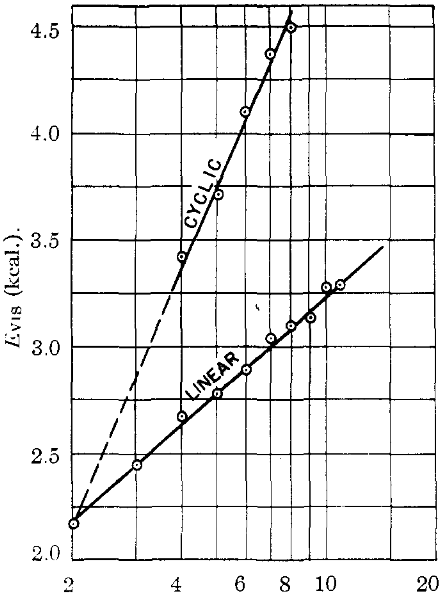

Fig. 5.—Energies of activation for viscous flow of linear and cyclic methylpolysiloxanes.

From the viscosities at 100° and 210°F., the values of E_{vis} and ln μ_∞ have been calculated, using the Arrhenius equation[7]

$$\eta_T = \eta_\infty e^{E_{vis}/RT} \qquad (12)$$

and these values are recorded in columns 4 and 5, Table II. The energy of activation for viscous flow, E_{vis}, is plotted in Fig. 5 against the number of units. It is a linear function of the logarithm of the number of units, the appropriate equations being

$$\text{Linear: } E_{vis} = 1.74 + 1.49 \log x \quad \text{(kcal.)} \qquad (13)$$
$$\text{Cyclic: } E_{vis} = 0.98 + 3.96 \log x \quad \text{(kcal.)} \qquad (14)$$

Using these linear relations, (10), (11), (13) and (14), together with (12), general equations for the viscosities of the linear and cyclic compounds may be derived in a manner analogous to that used in obtaining the vapor pressure relations. The resulting general equations are

$$\log \eta_L = -2.04 + \frac{380}{T} + \left[0.37 + \frac{326}{T}\right] \log x \qquad (15)$$
$$\log \eta_R = -2.13 + \frac{214}{T} - \left[0.04 - \frac{866}{T}\right] \log x \qquad (16)$$

The values of ln η_∞ in column 6, Table II, were calculated from (15) and (16) by setting $T = \infty$. Ln η_∞ is nearly constant for the cyclic compounds but varies over a wide range for the linear molecules. The viscosities of the cyclic compounds not only are higher than those of the corresponding linear compounds, but also increase more rapidly with molecular size.

Mixing two or more linear methylpolysiloxanes lowers the value of E_{vis} for the mixture below that for a single compound of the same average composition. Three examples are outlined in Table

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[7] S. Arrhenius, *Meddel. Vetenskapakad. Nobelinst.*, **3**, 20 (1916).

TABLE V

EFFECT OF MIXING ON E_{vis}

Molar composition of mixture	x av.	Viscosity, cp. 25°C.	Viscosity, cp. 75°C.	E_{vis}	E_{vis} (calcd.)
41.3% M_2D_4 58.7% M_2D_2	4.83	1.738	0.8914	2.75	2.76[a]
45.7% M_2D_4 54.3% D_6	6	3.470	1.583	3.24	3.54[b]
Oil: M_2D_{x-2}	3.7	1.20	...	2.31	2.59°

[a] Calculated by equation (13). [b] $0.457 \times 2.89 + 0.543 \times 4.10 = 3.54$.

V. The first, a mixture of a 4-silicon with a 6-silicon chain, shows a slight reduction in E_{vis} below that calculated from (13). The second, a mixture of a 6-silicon chain and a 6-silicon ring, has a value of E_{vis} considerably lower than that calculated by means of a linear relation between the molar composition and the E_{vis} values of the pure compounds. The third example is a low viscosity silicone oil comprising a mixture of linear compounds of average length 3.7 units. This mixture shows a marked negative deviation from equation (13).

The Unit of Flow

Eyring[8,9,10] and co-workers have demonstrated that for many molecules the standard free energy of activation for viscous flow, $\Delta F^{\ddagger}_{vis}$, is related to the energy of vaporization at the normal boiling point ΔE_{vap}, by the equation

$$\frac{\Delta E_{vap}}{\Delta F^{\ddagger}_{vis}} = 2.45 \tag{17}$$

and that for small molecules ΔE_{vap} is either three or four times the energy of activation for viscous flow, E_{vis}, the factor being three times for symmetrical, or nearly spherical, molecules, and four times for asymmetric or polar molecules. Eyring[10] shows that $\Delta F^{\ddagger}_{vis}$ is given by the relation

$$\Delta F^{\ddagger}_{vis} = RT \ln \frac{V\eta}{hN} \tag{18}$$

where V is the molar volume ($V = Mv$), h is the Planck constant and N is the Avogadro number. At $T = 100$°F., equation (18) may be rewritten as

$$\Delta F^{\ddagger}_{vis} = 3.43 + 1.43 \log [vM\eta] \tag{19}$$

at constant temperature and is then in convenient form for calculation. In Table VI, values of $\Delta F^{\ddagger}_{vis}$ calculated by means of equation (19) are tabulated. The values of E_{vis} are taken from Table II.

TABLE VI

RELATIONS BETWEEN FLOW AND VAPORIZATION ENERGIES

Compound	$\Delta F^{\ddagger}_{vis}$ (eq. 19)	E_{vis}	E_{vap}, kcal. (eq. 20)	$\frac{\Delta E_{vap}}{\Delta F^{\ddagger}_{vis}}$	$\frac{\Delta E_{vap}}{\Delta E_{vis}}$
D_4	4.47	3.42	9.96	2.21	2.89
D_5	4.95	3.71	11.2	2.26	3.02
D_6	5.40	4.10	12.5	2.32	3.05
D_7	5.75	4.37	13.8	2.40	3.16
D_8	6.03	4.50	15.1	2.51	3.36
M_2	3.36	2.17	7.19	2.14	3.31
M_2D	3.88	2.45	8.77	2.26	3.58
M_2D_2	4.30	2.67	10.4	2.42	3.90
M_2D_3	4.62	2.78	12.0	2.60	4.31
M_2D_4	4.86	2.89	13.6	2.80	4.70
M_2D_5	5.13	3.04	15.2	2.96	5.00
M_2D_6	5.27	3.10	16.8	3.19	5.41
M_2D_7	5.44	3.13	18.4	3.38	5.89
M_2D_8	5.59	3.27	20.0	3.58	6.11
M_2D_9	5.74	3.28	21.6	3.76	6.59

The energy of vaporization of each compound has been calculated from its heat of vaporization by means of the relation

$$\Delta E_{vap} = \Delta H_{vap} - RT_{b.p.} \tag{20}$$

where $RT_{b.p.}$ is given by

$$\text{Linear: } RT_{b.p.} = \frac{4620 + 1610x}{8.68 + x} \tag{21}$$

$$\text{Cyclic: } RT_{b.p.} = \frac{8920 + 2200x}{15.8 + x} \tag{22}$$

derived from (8) and (9) by setting $p = 760$ mm. The calculated values of ΔE_{vap} are recorded in Table IV, column 4. In the last two columns are the values of the ratios $\Delta E_{vap}/\Delta F^{\ddagger}_{vis}$ and $\Delta E_{vap}/\Delta E_{vis}$ for each compound.

The average value of the ratio $\Delta E_{vap}/\Delta F^{\ddagger}_{vis}$ for the cyclic compounds is 2.34, which is very nearly that found by Eyring and co-workers for many series of organic compounds. There appears, however, to be a uniform trend toward larger ratios for larger molecules. This trend is even more marked in the series of linear compounds, where the values range from 2.14 for M_2 to 3.76 for M_2D_9.

The ratios $\Delta E_{vap}/\Delta E_{vis}$ show the same trends. The ratio is about 3 for the cyclic compounds, indicating that these are approximately spherical molecules. The value of 3.3 for M_2 likewise indicates a nearly spherical molecule. The ratio increases rapidly with the length of the chain.

A similar increase in the ratio of ΔE_{vap} to E_{vis} above 4 has been observed in the hydrocarbon series by Kauzmann and Eyring.[11] They ascribe this behavior to the motion of the chain in segments, the activation energy for the movement of a segment being but a fraction of that required for the motion of the entire molecule. The size of the unit of flow for each molecule was estimated to be that of the member of the series for which ΔE_{vap} equaled four times the value of E_{vis} for the molecule in question. This type of calculation has been carried out for the linear methylpolysiloxanes with the results shown in Fig. 6, in which the size of the unit of flow is plotted as a function of the size of the molecule.

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(8) Powell, Roseveare and Eyring, *Ind. Eng. Chem.*, **33**, 430 (1941).

(9) Ewell and Eyring, *J. Chem. Phys.*, **5**, 726 (1937).

(10) Glasstone, Laidler and Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(11) W. Kauzmann and H. Eyring, THIS JOURNAL, **62**, 3113 (1940).

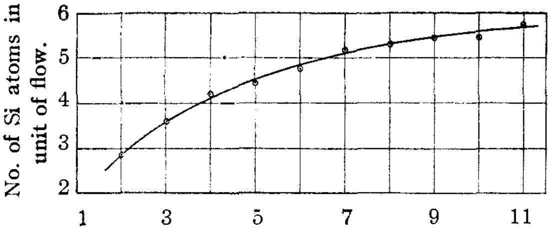

Fig. 6.—The unit of flow in linear methylpolysiloxanes.

Kauzmann and Eyring estimate that the average length of the unit of flow for very long hydrocarbon chains becomes constant for molecules longer than 20 to 25 carbon atoms. From Fig. 6, the unit of flow for methyl silicones is seen to approach a constant size of approximately 6 silicon atoms. As a check on this figure, the value of E_{vis} for high molecular weight silicone oils, which are predominantly linear, approaches asymptotically the value of 3.8 kcal. as the viscosity is increased.[12] This value of E_{vis} indicates a limiting flow unit 7.2 silicon atoms in length, which compares well with the estimate made above.

The relative sizes of the hydrocarbon and silicone oil flow units are compared in Table VII. The sizes are based on the extended form of the chains, and for the silicone units the covalent oxygen angle was assumed.

TABLE VII

COMPARISON OF HYDROCARBON AND SILICONE UNITS OF FLOW

	Hydrocarbon	Silicone
Composition	$C_{22}H_{50}$	$(CH_3)_{14}Si_7O_7$
Molecular weight	350	519
Length, Ångströms	32	23
Cross-section, Å. sq.	4 × 5	5 × 8
Volume. Å. cubed	640	920
E_{vis}, kcal.	6-7	3.8

The two flow units are roughly the same size. However, both the weight and volume of the silicone unit are about fifty per cent. greater than the weight and volume of the hydrocarbon unit, while the activation energy for viscous flow of the hydrocarbon unit is seventy per cent. greater than that of the silicone unit. If one accepts the concept that the activation energy E_{vis} represents the energy necessary to form a hole large enough to accommodate the unit of flow, then methyl silicone oils provide larger holes for a lesser expenditure of energy than do hydrocarbons. Thus, the attractive forces between molecules in the liquid state are lower in methyl silicone oils than in hydrocarbons, a fact which also is demonstrated by the low boiling points of methyl silicones compared to those of hydrocarbons of equivalent molecular weight.

Acknowledgment.—The author is indebted to Dr. Winton Patnode for furnishing many of the compounds studied and to Dr. R. O. Sauer for his advice on analysis. Thanks are due Miss B. Sullivan for determining the viscosities.

Summary

The linear methylpolysiloxanes with 7, 8, 9, 10 and 11 silicon atoms have been isolated, and their viscosity and vapor pressure curves have been determined. The vapor pressure curves of the shorter linear compounds and of the cyclic compounds up to D_8 have been determined.

Simple relations have been found which express vapor pressure and viscosity as functions of temperature and composition. For linear molecules these are:

$$\log p_L = 6.28 - \frac{1030}{T} + \left[0.443 - \frac{360}{T}\right] x \quad (x \geqslant 5)$$

$$\log \eta_L = -2.04 + \frac{380}{T} + \left[0.37 + \frac{326}{T}\right] \log x$$

and for cyclic molecules

$$\log p_R = 7.07 - \frac{1190}{T} + \left[0.265 - \frac{294}{T}\right] x$$

$$\log \eta_R = -2.13 + \frac{214}{T} - \left[0.04 - \frac{866}{T}\right] \log x$$

where x is the number of silicon-containing units.

By comparing the energy of vaporization with the activation energy for viscous flow, the unit of flow in high molecular weight silicone polymer fluids has been estimated to be $(CH_3)_{14}Si_7O_7$. This is somewhat larger than the unit of flow in hydrocarbons, as estimated by Eyring and coworkers. Since the energy of activation for viscous flow is smaller for silicones, it is concluded that the attractive forces between molecules in liquid linear polysiloxanes are much lower than those in hydrocarbons of comparable molecular weight.

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[12] E_{vis} is 3.70 kcal. for an oil with a viscosity of 50 centistokes at 100°F., and 3.79 kcal. for an oil with a viscosity of 1000 centistokes.