to long chain polymer in other systems. In fact, there is some evidence that diradicals from 1,4,5-oxadithiacycloheptane can be the source of polymer of high molecular weight. Photopolymerization of the pure ring compound can be induced by irradiation with ultraviolet light, and if no linear disulfide is present, the reaction presumably proceeds by a diradical mechanism. There is also evidence that, upon irradiation, solutions of 1,4,5-oxadithiacycloheptane in styrene polymerize somewhat more rapidly than pure styrene, in contrast with the results described for methyl methacrylate. An important factor influencing the relative amounts of rings and chains which will be formed in any given case is the steric situation governing ring formation.

Zimm and Bragg[3] have suggested that diradicals produced in thermal polymerization can transfer with monomer to give two monoradicals, and that these monoradicals then grow to give the high polymer observed in the thermal polymerization of styrene. Experimental work with styrene containing substances with high transfer constants does not confirm this suggestion. Mayo, Gregg and Matheson[10] have shown that the addition of 10% carbon tetrachloride to styrene has an effect on the rate which can be explained by the dilution effect. We have measured the rate of polymerization of styrene in the presence of 0.2% *n*-octyl mercaptan and shown that it is a few per cent. less than the rate with pure styrene. Zimm's mechanism would have predicted a considerable increase in rate in both these cases, since the rate of transfer to the carbon tetrachloride or the octyl mercaptan would be far greater than the rate of transfer to monomer.

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PRINCETON, N. J.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Physical Properties of Organosilicon Compounds. III. Thermodynamic Properties of Octamethylcyclotetrasiloxane

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The measured vapor pressures of liquid octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$, obey the equation $\log_{10} P_{\text{mm}} = 45.7216 - (4530.2/T) - 12.3508 \log_{10} T$. The enthalpy of vaporization, ΔH_v, as a function of absolute temperature may be represented as: $\Delta H_v = 20.7 - 0.0245T$ kcal. mole^{-1}. Activities of $[(CH_3)_2SiO]_4$ in a high molecular weight silicone oil have been determined by measurements of vapor pressure. The polymer–solvent interaction parameter, μ, has a mean value of 0.28 for this system. The constants of Berthelot's equation of state for $[(CH_3)_2SiO]_4$ have been evaluated from approximate values of the critical constants. The true melting point of pure octamethylcyclotetrasiloxane was found to be 17.65°.

Introduction

In a previous study[1] the physical properties of octamethylcyclotetrasiloxane, $\{[(CH_3)_2SiO]_4\}$ (I), have been partially described. In the present paper, the vapor pressure of I has been re-evaluated as a function of temperature and the enthalpy of vaporization has been shown to be strongly temperature-dependent. Since little is known concerning systems containing polydimethylsiloxanes and I, it was of interest to determine the vapor pressures of solution of silicone oil in I and in this fashion to estimate the polymer–solvent interaction parameter.

Experimental

The hydrolysis of dimethyldichlorosilane[2,3] yielded crude I upon distillation. This crude product was then dried over calcium hydride and distilled again, yielding I; $n^{20}\text{D}$ 1.3968; b.p. 175 ± 1°. This product was then further purified by several times partially freezing and discarding the liquid phase.[4] The product resulting from this treatment was frozen and warmed very slowly while measuring the temperature *vs.* time employing a platinum resistance thermometer (calibrated by the National Bureau of Standards) in conjunction with the Leeds and Northrup G-2 Mueller temperature bridge. In this manner the warming curve through the melting range was obtained. An algebraic test of Taylor and Rossini[5] indicated that thermodynamic equilibrium existed between the solid and liquid phase during melting. Employing the usual assumptions that the rate of melting is constant after *ca.* one-half of the sample is melted and that all the impurity exists in the liquid phase, the true melting point of pure I was calculated to be 17.65°.[6,7] The actual melting point of the present sample was found to be 17.58°. Using the freezing point depression constant for I, $K_F = 38.0$ deg.,[1] a purity of 99.82 mole per cent. was estimated for this material.

A study of the vapor pressure of I as a function of temperature was initiated primarily because the previously reported relation[8] was based upon measurements at only two temperatures. A modified isoteniscope of Smith and Menzies[9,10] was used in the measurement of the vapor pressures using the method previously described[1] for control and measurement of the temperature. A portion of the sample of I (purified as described above) was repeatedly outgassed and finally introduced into the isoteniscope by vacuum distillation. Some observed and calculated values of the vapor pressure of I are presented in Table I.

The constants of equation 1 were determined by application of the method of selected points.

$$\log_{10} P_{\text{mm}} = 45.7216 - \frac{4530.2}{T} - 12.3508 \log_{10} T \quad (1)$$

Equation 1 reproduced the observed vapor pressures of liquid I, P_{mm}, with a mean deviation of 0.1 mm. The solution of equation 1 at 760 mm. yielded a value of 176.4° for the normal boiling point (previous value 175.8° at 758 mm.[8]).

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TABLE I

VAPOR PRESSURE OF LIQUID OCTAMETHYLCYCLOTETRASILOXANE AT VARIOUS TEMPERATURES[a]

t, °C.	P_{mm} Obsd.	P_{mm} Calcd.[b]	t, °C.	P_{mm} Obsd.	P_{mm} Calcd.
30.4	1.5	1.3	99.9	65.4	65.5
42.4	3.2	3.2	104.8	79.0	79.6
49.2	4.9	4.9	116.7	124.5	126.3
53.6	6.3	6.4	123.2	159.6	159.6
62.8	10.9	10.9	134.8	236.1	236.8
72.8	18.6	18.6	139.6	275.6	277.3
83.7	31.9	31.8	149.7	372.8	372.8
93.5	49.7	49.7	155.3	439.7	437.9

[a] The observed values of the vapor pressures above 80° were corrected for the vapor pressure of mercury at each temperature. A total of three different runs employing individual samples of I were carried out and data from each were used to evaluate the constants for equation 1. [b] From equation 1.

By differentiating 1, the enthalpy of vaporization of I, ΔH_V, as a function of the absolute temperature, T, may be represented by

$$\Delta H_V = 20.7 - 0.0245T \text{ kcal. mole}^{-1} \qquad (2)$$

Selected values of the enthalpy of vaporization at various temperatures are presented in Table II.

TABLE II

THE ENTHALPY OF VAPORIZATION OF OCTAMETHYLCYCLOTETRASILOXANE AT VARIOUS TEMPERATURES

Temp., °C.	ΔH_V, kcal. mole^{-1}	$\Delta H_V'$, kcal. mole^{-1}[a]
25	13.4	13.4
100	11.6	11.5
125	10.9	10.7
175	9.7	9.0

[a] $\Delta H_V'$ is the enthalpy of vaporization of I corrected for non-ideality of the vapor (*vide infra*) and for the liquid volume which is ignored in the Clausius–Clapeyron equation.

The critical temperature of I, T_C, was measured directly by observing the disappearance of the meniscus in thick-walled Pyrex capillaries containing various volume fractions of liquid. A value of $T_C = 587 \pm 2$°K. (*i.e.*, 314 ± 2°) was obtained in this way. Using the law of rectilinear diameters, together with the density data of Hurd[11] for I, the critical density was found to be 0.31 g. ml.$^{-1}$ (the critical volume, V_C, is then 954 ml. mole^{-1}). A well known relation among the critical constants, $P_C = 0.27\ (RT_C/V_C)$ (where P_C is the critical pressure and R is the gas constant), yields $P_C = 14$ atm.[12] The Berthelot equation of state for I was found to be

$$PV = RT + 2.42 \times 10^2 \left(1 - \frac{2.07 \times 10^6}{T^2}\right)P \qquad (3)$$

in units of cm.^{3} atm. The fugacity corrections in this paper have all been calculated by means of equation 3.

The rather large variation of ΔH_V with temperature, indicated by the data of Table II, reflects the difference of 24.5 cal. mole^{-1} between the heat capacities of the vapor and the liquid. For the sake of comparison, the values of $C_p^l - C_p^v$ (where C_p^l is the molar heat capacity of the liquid at constant pressure and C_p^v is the molar heat capacity of the vapor at constant pressure) for several aliphatic hydrocarbons have been calculated using liquid heat capacities[13] and estimating the vapor heat capacities at 27° from an approximate equation developed by Parks and Huffman.[14] Values of $C_p^l - C_p^v$ for several hydrocarbons and I are listed in Table III.

TABLE III

$C_p^l - C_p^v$ AS A FUNCTION OF MOLECULAR WEIGHT AT 27°

Compound	Mol. wt.	$C_p^l - C_p^v$, cal. deg.$^{-1}$ mole^{-1}
n-C_8H_{18}	114.2	14.4
n-$C_{10}H_{22}$	142.3	18.5
n-$C_{12}H_{26}$	170.3	22.5
n-$C_{14}H_{30}$	198.4	26.2
$[(CH_3)_2SiO]_4$	296.6	24.5

It is apparent that $C_p^l - C_p^v$ (*i.e.*, the temperature coefficient of ΔH_V) increases with increasing molecular weight in a homologous series. Failure to observe with hydrocarbons the large variation of ΔH_V with temperature which has been found with I may be attributed to lack of adequate vapor pressure data; this is especially true for hydrocarbons containing more than twelve carbon atoms.

It was of interest to calculate the value of the solubility parameter[15] of I at 25°, δ_{25}, from the enthalpy of vaporization. It was found that $\delta_{25} = 6.4$ as calculated in the usual fashion.[15] In order to obtain another estimate of δ_{25}, the relation $\delta_{25} = 4.1[\gamma_{25}/(V_{25})^{1/3}]^{0.43}$[15] was used in which V_{25} is the molar volume and γ_{25} is the surface tension at 25°. The surface tension of I at 25° was found to be 17.3 dynes cm.$^{-1}$ employing the twin capillary method of Mills and Robinson.[16] This value of γ_{25} is in excellent agreement with the previously reported value.[3] If then V_{25} is calculated from the data of Hurd,[11] one may calculate δ_{25} to be 6.2 in good agreement with the value determined from the energy of vaporization.

The polymeric fluid to be used in the study of the vapor pressure of solutions of polymer in I, was prepared by acid equilibration.[2] To 500 cm.^{3} of I was added 6 cm.^{3} of hexamethyldisiloxane (n^{20}_D 1.3775) and four weights per cent. of sulfuric acid. After a 48-hour equilibration period (with vigorous agitation) the polymeric silicone fluid was treated with distilled water, separated, washed and finally dried over anhydrous sodium carbonate. This material was then thoroughly devolatilized at 140° by long pumping. The vapor pressure of the resulting oil II at 140° was found to be 0.05 mm. and the viscosity at 25° was found to be 181.6 centipoises; n^{20}_D 1.4053, d^{25}_4 0.9660 g. ml.$^{-1}$. If one employs the Flory relationship for melt viscosities,[17,18] the molecular weight of the devolatilized fluid may be estimated to be 10,700. In toluene solution, an intrinsic viscosity of 0.090 was obtained for II corresponding to a molecular weight of 10,100[18] in good agreement with the value obtained from the melt viscosity. Thus, II corresponds to

$$(CH_3)_3SiO[(CH_3)_2SiO]_{115}Si(CH_3)_3$$

The experimental procedure involved in the determination of the vapor pressures of solution of II in I, consisted of first determining the weight of II sealed into a modified isoteniscope.[19] Then small increments of I were added by vacuum distillation. The composition of the resulting solution was then determined by weighing the isoteniscope and contents; finally, the vapor pressure of the solution was measured at 140 ± 0.2° in the conventional manner. A total of four individual runs was made. These data are summarized in Table IV.

Huggins[20,21] has shown that for polymer solutions

$$\ln \frac{P}{P} = \ln \phi_0 + \left(1 - \frac{1}{\overline{M}_n}\right)\phi_p + \mu\phi_p^2 \qquad (4)$$

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(13) "International Critical Tables," Vol. V, p. 113.

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(17) P. J. Flory, THIS JOURNAL, **62**, 1057 (1940).

(18) A. J. Barry, *J. Applied Phys.*, **17**, 1020 (1946).

(19) It has been noted previously that silicon-containing compounds dissolve large amounts of air, *cf.*, W. T. Grubb and R. C. Osthoff, THIS JOURNAL, **75**, 2230 (1953). In the case of II about 20 outgassings were required to remove dissolved air. The reservoir of I contained anhydrous sodium sulfate and was not exposed to the atmosphere after the original outgassing had been accomplished.

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TABLE IV

VAPOR PRESSURE OF SOLUTIONS OF POLYDIMETHYLSILOXANE IN OCTAMETHYLCYCLOTETRASILOXANE AT 140°

Weight % I		Vapor pressure, mm.	Fugacity,[a] mm.
Run A	6.75	59.6	59.3
	40.6	245.7	239.6
	54.8	260.1	253.1
Run B	45.9	247.5	241.3
	62.1	257.3	250.4
	70.4	273.1	265.5
	80.7	275.0	267.3
	83.9	276.8	268.8
Run C	12.7	94.7	93.8
	20.6	150.8	148.4
	25.4	170.8	167.7
	37.7	222.0	216.9
Run D	10.2	82.5	81.8
	19.0	132.9	131.0
	32.6	211.6	206.9

[a] The fugacities were calculated from the Berthelot equation of state for I (equation 3).

where

P is the vapor pressure of the soln.
P_0 is the vapor pressure of the pure solvent
ϕ_0 is the vol. fraction of solvent
ϕ_p is the vol. fraction of polymer
$\bar{M}_n$ is the number av. mol. wt.
μ is the polymer–solvent interaction parameter

The representation of the present data by means of equation 4 was facilitated by the fact that $1/\bar{M}_n$ was sufficiently small to be neglected in calculation. The density of II at 140° was found to be 0.8673 g. ml.$^{-1}$ and the assumption of volume additivity of solutions of II in I was shown to be valid within 0.05%. In calculations based on equation 4, the volume fractions were also corrected for the vapor volume of I at 140°. Thus from the smoothed data, the mean value of μ was found to be 0.28. Using this value of μ, at various volume fractions, the values of f/f_0 (the ratio of fugacities) were calculated from equation 4. These values together with the values of $\Delta\bar{F}_0$, the partial molal free energy of mixing, are presented in Table V.

TABLE V

OBSERVED AND CALCULATED VALUES OF f/f_0 AND P/P_0 FOR VARIOUS VOLUME FRACTIONS AT 140°

ϕ_0	ϕ_p	P/P_0 (obsd.)	f/f_0 Obsd.	f/f_0 Calc	$-\Delta\bar{F}_0$, cal. mole^{-1}
0.1	0.9	0.260	0.265	0.309	1093
.2	.8	.505	.512	.532	552
.3	.7	.700	.705	.692	287
.4	.6	.832	.837	.876	148
.5	.5	.906	.908	.884	79.4
.6	.4	.945	.947	.936	45.2
.7	.3	.972	.974	.970	22.7
.8	.2	.990	.991	.989	7.5
.9	.1	.999	.999	.998	0.8
1.0	.0	1.000	1.000	1.000	0.0

In Fig. 1, the experimental points and the curve calculated by means of equation 4 (for μ = 0.28) are presented. It will be observed that reasonable agreement is obtained considering the experimental difficulties.[22-24] The fugacity correction has been applied in the manner described previously. Compared to the experimental uncertainty, this correction is not significant at 140°, but would become important at higher pressures of I.

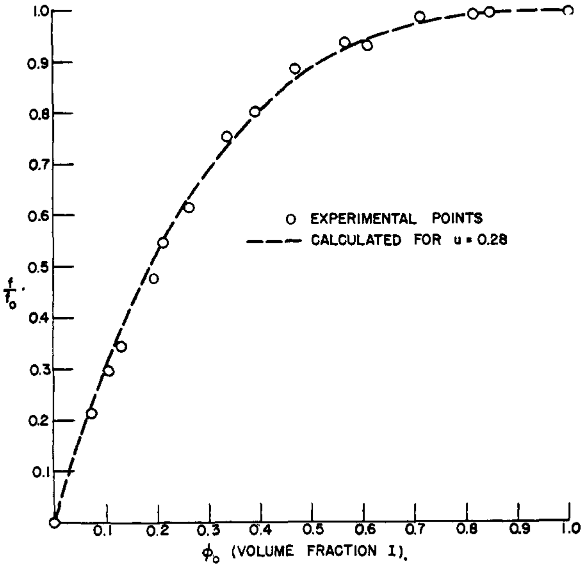

Fig. 1.—Relative fugacity of solutions of I in II as a function of concentration of I.

In order to determine the validity of applying the preceding results at temperatures other than 140°, a direct measurement was made of the enthalpy of mixing (ΔH^m) of I with a low viscosity polydimethylsiloxane fluid. If ΔH^m is zero, then both μ and $\Delta\bar{F}_0$ for I and II will be temperature independent. Newing[25] has shown that the enthalpy of mixing of a silicone fluid with benzene at 25° has a maximum value of −1.1 cal. ml.$^{-1}$ when equal volumes of the two components are mixed. This value is practically independent of the molecular weight of the fluid. In the present determination, 200 ml. each of I and polydimethylsiloxane fluid having a viscosity of 20 centistokes at 25° were charged into a calorimeter consisting of a dewar flask separated into two concentric compartments by means of a large diameter glass tube inserted into a pool of mercury. Temperature was measured to ±0.01° by a two-junction copper–constantan thermocouple using a Leeds and Northrup recording potentiometer. Employing a motor-driven stirrer operating at constant rate, the two liquids were mixed by raising the glass tube. The heat capacity of the system was estimated by mixing equal volumes of 20 centistoke silicone fluid with benzene using Newing's value, $\Delta H^m = -1.1$ cal. ml.$^{-1}$. The heat of mixing of I with II was found to be $\Delta H^m = 0.00 \pm 0.01$ cal. ml.$^{-1}$. Since $\Delta H^m = V_m (\delta_0 - \delta_p)^2\phi_0\phi_p$[26] and $\delta_0 = 6.4$ cal.$^{1/2}$ cm.$^{-3/2}$ for I, the value of the solubility parameter of the polymer, δ_p, must be very near to 6.4 cal.$^{1/2}$ cm.$^{-3/2}$ and independent of molecular weight.

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