Specific Volumes of Dimethylsiloxane Polymers to 900 Bars

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ABSTRACT: Volumetric data are reported for seven dimethylsiloxanes of different molecular weight in the region 25–70°C and at pressures to 900 bars. Tait equation coefficients are given to represent the PVT data. The parameters for Flory's equation of state are determined and their dependence on molecular weight is discussed.

Specific-volume data, as a function of temperature and pressure, are required for evaluation of reduction parameters in equations of state for liquids.[1–4] In the last decade, it has become common practice to use an equation of state of the van der Waals type, proposed by Flory,[5] in the treatment of mixtures.

In this work we studied the applicability of Flory's equation to volumetric properties of some dimethylsiloxanes. Toward that end, we have obtained experimental data at pressures to 900 bars for the specific volumes of hexadimethylsiloxane (HMDS) and six poly(dimethylsiloxanes) (PDMS) of different molecular weight. These siloxanes were recently used in calorimetric studies[6] of polymer solutions; the pure component data presented here are needed for theoretical interpretation of the polymer–solution data.

Experimental Section

For high-pressure studies, the experimental equipment is the same as that used by Beret;[7] the central component is a high-pressure cell with a flexible bellows to contain the sample and to isolate it from the pressure-transmitting fluid.[8] The apparatus is calibrated with highly accurate PVT data for mercury and *n*-heptane.[7]

Pressures are measured with a precision Heise gauge whose accuracy is 0.1% of full scale (±1 bar).

The high-pressure cell is located in a constant-temperature bath using silicone oil as heating fluid. The bath is controlled to within ±0.01 °C by a Hallikainen proportional temperature controller. Calibrated thermometers, used for temperature measurements, are accurate to within ±0.05 °C.

Taking into consideration errors in temperature and pressure measurements as well as errors in calibration, the overall uncertainty of our relative-volume measurements is 0.08%.

For measuring specific volumes at atmospheric pressure, a conventional glass dilatometer was used. The dilatometer was calibrated with mercury at 22 and 70 °C. Readings of the meniscus in the capillary were made with a cathetometer to ±0.5 mm. The calibrated dilatometer was tested with carefully degassed *n*-dodecane. In the temperature range 22 to 72.5 °C, measured results agreed with those reported by Rossini[9] to within better than ±0.01%. The maximum deviation was 3×10^{-4} cm^3/g.

Materials. Characteristics of the PDMS samples are shown in Table I. HMDS was of purity greater than 99% as obtained from the supplier (Fluka) and was used without further purification. All PDMS samples, characterized by the viscosity as reported by the supplier, have a narrow molecular weight distribution. Drying at elevated temperatures under vacuum did not yield any weight change, i.e., the PDMS samples were solvent free.

Results

Measurements extend to 900 bars and cover the temperature range 25 to 70 °C. Detailed experimental results are available as supplementary material; we report here only a summary.

Measurements at low pressure are represented by the empirical equation

$$v_{sp}^0 = A^{(1)} + A^{(2)}t + A^{(3)}t^2 \tag{1}$$

where v_{sp}^0 is in cm^3/g and t is in °C. Coefficients $A^{(1)}$, $A^{(2)}$, and $A^{(3)}$ are shown in Table II. The final column in Table II shows that eq 1 reproduces the experimental data within experimental uncertainty.

Figure 1 shows experimental results at atmospheric pressure for the different PDMS. Also shown are results for HMDS obtained previously.[10]

Measurements at high pressure are represented by a modified Tait equation:[7,8c]

$$v_{sp}/v_{sp}^0 = 1 - c \ln\left[1 + \frac{P}{b^{(1)}\exp(-b^{(2)}t)}\right] \tag{2}$$

where v_{sp} is the specific volume at pressure P and v_{sp}^0 is the specific volume at zero pressure. Temperature t is in degrees centigrade and the pressure is in bars. Tait coefficients are given in Table III. For all siloxanes $c = 0.0894$ which also was used by Simha et al.[8c] for high molecular weight hydrocarbons and for several polymers. The last column in Table III shows that eq 2 represents the data within the experimental accuracy except for HMDS and PDMS 3. Using a three-parameter Tait equation for these two liquids, allowing c to be an adjustable parameter, yields only a little improvement in the standard deviation. It appears that for these highly compressible, low molecular weight siloxanes the Tait equation is not flexible enough to represent PVT data within the experimental error.

Figures 2 and 3 show the effect of pressure on volume for various temperatures. It is clear that eq 2 does not represent well data for HMDS and PDMS 3.

Dependence on Molecular Weight. Figure 1 shows that with increasing molecular weight, the specific volume v_{sp} at atmospheric pressure becomes smaller; also, its temperature dependence decreases. For $\overline{M}_n \gtrsim 6000$, v_{sp} and its temperature dependence become independent of molecular weight. This follows from the experimental results for PDMS 350 and PDMS 1000, which agree with each other within the experimental error (±0.01%). Further, these results agree within 0.07% with those reported by Flory et al.[11] Flory et al. have used a PDMS with a viscosity average molecular weight, $\overline{M}_v \sim 10^5$. As they removed low molecular weight constituents by fractional precipitation, the molecular weight distribution of their PDMS is expected to be narrow. Hence the number average molecular weight $\overline{M}_n$ of their PDMS is much larger than those of the PDMS used in this work. The independence of v_{sp} of molecular weight explains why Table II gives the same coefficients $A^{(1)}$, $A^{(2)}$, and $A^{(3)}$ for PDMS 350 and PDMS 1000.

Figure 4 shows the dependence of the density ρ on molecular weight. In addition to the results obtained in this work, Figure 4 shows densities for octamethyltrisiloxane (trimer) and dodecamethylpentasiloxane (pentamer) reported by Patterson et al.[12] and for PDMS from Flory et al.[11] All densities correlate well with molecular weight. With increasing $\overline{M}_n$, the density increases. This observation is physically reasonable because the higher the molecular weight, the higher is the number of chemical bonds per unit volume, an effect that raises the

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Table I
Polymer Characteristics

Substance and source	$\overline{M}_n{}^a$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n{}^b$	$\eta_{20°C}$, cP^c
HMDS, Fluka AG	162.38	162.38	1.00	
PDMS 3, Goldschmidt AG	594	665	1.12	3
PDMS 10, Goldschmidt AG	958	1418	1.48	10
PDMS 20, Goldschmidt AG	1540	1879	1.22	20
PDMS 100, Goldschmidt AG	4170	5921	1.42	100
PDMS 350, Goldschmidt AG	6560	11218	1.71	350
PDMS 1000, Goldschmidt AG	7860	17056	2.17	1000

[a] Vapor pressure osmometry. [b] GPC perfomed by DeBell & Richardson Inc., Enfield, Conn., 06082. [c] Reported by supplier.

Table II
Specific Volumes at Low Pressure[a]

Substance	$A^{(1)}$	$A^{(2)} \times 10^3$	$A^{(3)} \times 10^6$	$\sigma(v_{sp}{}^0) \times 10^4$, cm^3/g^b
HMDS	1.27438	1.58144	4.77777	0.11
PDMS 3	1.07411	1.23519	0.452937	0.74
PDMS 10	1.05319	1.10547	0.362133	0.57
PDMS 20	1.02783	1.07383	−0.060039	0.20
PDMS 100	1.01000	1.04600	−0.307921	0.88
PDMS 350	1.00576	0.993072	−0.078064	0.32
PDMS 1000	1.00576	0.993072	−0.078064	0.32

[a] Coefficients in eq 1. [b] σ = standard deviation.

Table III
Specific Volumes at High Pressures[a]

Substance	c	$b^{(1)}$, bar	$b^{(2)} \times 10^3$, °C^{-1}	$\sigma(v_{sp}/v_{sp}{}^0) \times 10^4$ ^{b}
HMDS	0.0894	574	10.16	18
PDMS 3	0.0894	728	7.444	9.4
PDMS 10	0.0894	812	6.865	7.2
PDMS 20	0.0894	847	6.487	6.5
PDMS 100	0.0894	874	5.985	5.8
PDMS 350	0.0894	885	6.100	5.9
PDMS 1000	0.0894	885	6.100	5.9

[a] Coefficients of eq 2. [b] σ = standard deviation.

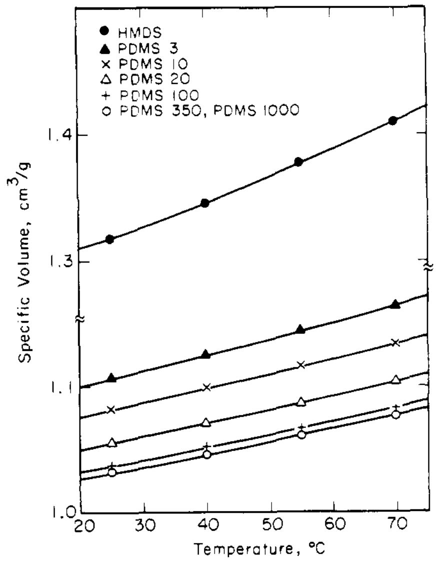

Figure 1. Temperature dependence of the specific volume at atmospheric pressure: (—) from eq 1.

density. At $\overline{M}_n \sim 6000$, it appears that the maximum number of chemical bonds per unit volume is reached; therefore, further increase in $\overline{M}_n$ does not change the density.

Figures 2 and 3 indicate that the effect of pressure on volume becomes decreasingly smaller with increasing molecular weight; for $\overline{M}_n \gtrsim 4200$, the relative volume is independent of the molecular weight. At higher temperatures, the effect of pressure is stronger and its dependence on molecular weight is more significant. This observation is physically reasonable because higher molecular weight produces a higher density and consequently a reduction of the compressibility at a given temperature. An increase in temperature lowers the density and thereby raises the compressibility.

Figure 5 shows a comparison between our data for HMDS and PDMS 1000 at 25 °C and those in the literature.[7,13] For HMDS the agreement is good for all pressures within the experimental error. Data by Beret et al.[7] for PDMS show a maximum deviation of ±0.07% at 900 bars, although their PDMS had a number average molecular weight of $\overline{M}_n \sim 47200$. This confirms our claim that the relative volume is independent of molecular weight for $\overline{M}_n \gtrsim 4200$, as discussed above.

Characteristic Parameters of Flory's Equation. As discussed elsewhere,[5] Flory's equation relates reduced pressure $\tilde{P}$ to reduced volume $\tilde{v}$ and reduced temperature $\tilde{T}$ by

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{v}\tilde{T}} \tag{3}$$

where $\tilde{P} = P/P^*$, $\tilde{v} = v/v^*$, and $\tilde{T} = T/T^*$; the quantities with an asterisk indicate the characteristic parameters. For pure liquids, the characteristic parameters can be determined from volumetric data in several ways. One method is to determine them from data at (essentially) zero pressure for density, thermal expansion coefficient α, and thermal pressure coefficient γ ($\alpha = (1/v)\,(\partial v/\partial T)_p$ and $\gamma = (\partial P/\partial T)_v$). This method is used by Flory et al.[14]

The advantage of Flory's method is that only data at atmospheric pressure are required. However, very accurate experimental values of α and γ data are necessary and these are often not available. Further, when determined by this method, the parameters are temperature dependent.

We fitted all PVT data presented in this work to eq 3 to determine the three parameters. Table IV shows the parameters for the seven dimethylsiloxanes. The last column of this table shows that the Flory equation represents all PVT data with a standard deviation of at most ±0.3%. Although this deviation is larger than our estimated experimental uncertainty, representation of the data with the Flory equation is good. Better agreement can be obtained by letting the parameters v^*, T^*, and P^* be functions of temperature. Temperature-dependent parameters can be calculated from the low-pressure data of this work. When that is done, the results indicate that the parameters given in Table IV are average values over the temperature range considered here. As the overall agreement with these average values is already satis-

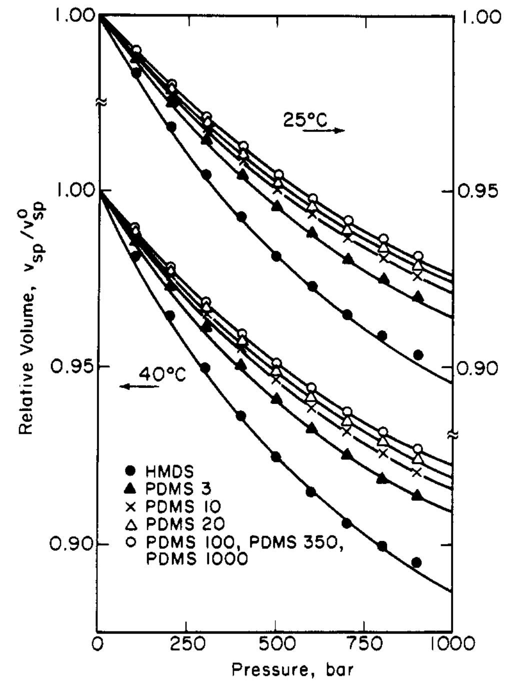

Figure 2. Pressure dependence of the relative volume at 25 and 40 °C: (—) from eq 2.

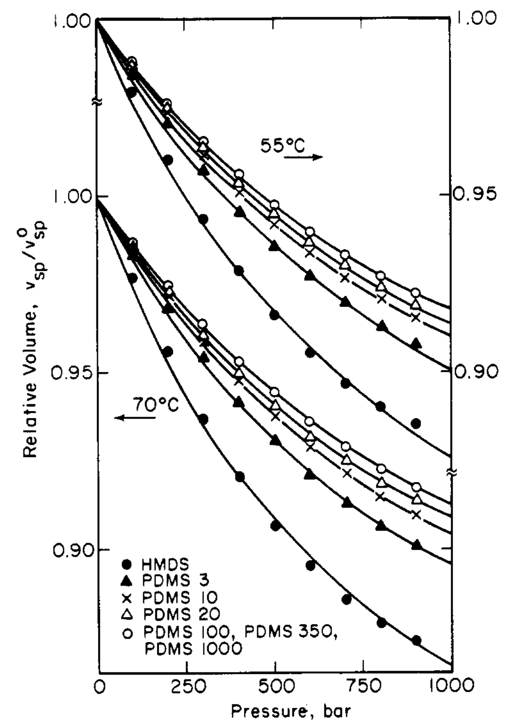

Figure 3. Pressure dependence of the relative volume at 55 and 70 °C: (—) from eq 2.

factory, we prefer to use these rather than temperature-dependent values.

With increasing molecular weight, we observe a systematic decrease in v^* and a systematic increase in T^*; similar results for other oligomers were reported by Simha and Havlik.[15] For P^* such a systematic change is not obtained; P^* remains nearly constant. For $\overline{M}_n \gtrsim 6000$, all parameters become independent of molecular weight as indicated by the same values for PDMS 350 and PDMS 1000. The decrease of v^* and the increase of T^* for $\overline{M}_n < 6000$ are consistent with results reported by Flory et al.[1a] for hydrocarbons, $H(CH_2)_nH$, with n varying from 6 to ∞ (linear polymethylene). For $n \gtrsim 300$, i.e., a molecular weight $\gtrsim 5000$, the parameters remain constant with further increase of n. However, in contrast to our results, Flory et al. found a systematic increase of P^* with increasing molecular weight; on the other hand, Patterson et al.[2] report a constant P^* for hydrocarbons from butane to polymethylene using Prigogine's principle of corresponding states for chain-molecule liquids. Flory et al. have obtained all their parameters from low-pressure data only; therefore, they could not determine the effect of pressure. From our results it seems that the effect of pressure on parameter P^* cancels the effect of molecular weight, whereas the parameters v^* and T^* are not seriously affected by pressure.

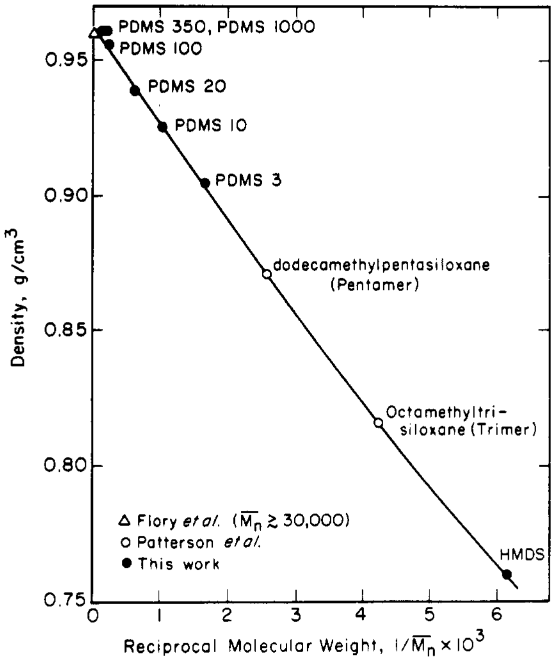

Figure 4. Dependence of density on the number-average molecular weight at 25 °C and 1 bar.

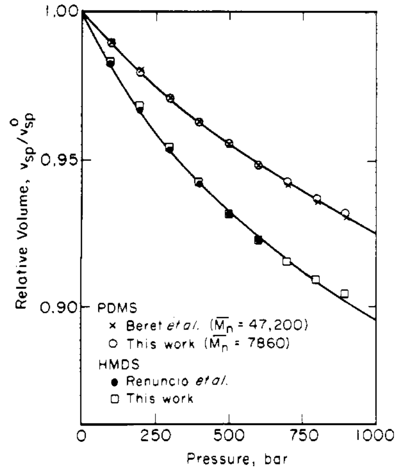

Figure 5. Comparison of relative volumes for HMDS and PDMS at 25 °C: (—) from eq 2.

Conclusion

The volumetric measurements obtained in this work show that while the Tait equation is useful for high molecular weight liquids, it cannot represent PVT data of the highly

Table IV
Parameters in Flory's Equation of State

Substance	v^*, cm^3/g	T^*, K	P^*, bar	$\sigma(v_{sp}) \times 10^4$,[a] cm^3/g
HMDS	0.9995	4468	3253	33
PDMS 3	0.8780	5070	3078	23
PDMS 10	0.8694	5288	3133	20
PDMS 20	0.8531	5395	3156	18
PDMS 100	0.8412	5470	3230	19
PDMS 350	0.8403	5554	3115	18
PDMS 1000	0.8403	5554	3115	18

[a] σ = standard deviation.

compressible liquids, HMDS and PDMS 3, within the experimental accuracy. Flory's equation of state represents well the PVT behavior of all liquids with characteristic parameters determined using all PVT data reported here. Equation-of-state parameters evaluated from volumetric data at 1 bar only differ significantly from those in Table IV and do not allow good representation of the data at high pressures. Although agreement between fitted and experimental PVT data is good, the deviations may be significant for polymer–solution thermodynamics since equation-of-state contributions may be important in calculating excess functions of polymer mixtures. We made no attempt to test other equations of state for polymer liquids.

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Supplementary Material Available: Experimental results for specific volume and relative volume at 25, 40, 55, and 70 °C at pressures to 900 bars for all seven dimethylsiloxanes in this work (8 pages). Ordering information can be found on any current masthead page.

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Excluded Volume Effect on the Principal Components of Polymer Chains. 1

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ABSTRACT: The excluded volume effect on the principal components is discussed by a perturbation method with the aid of a method of second quantization introduced by Fixman. The perturbation series of the excluded volume parameter z for the square radius of gyration is decomposed, up to the term linear in z, into the three orthogonal components along the principal axis of inertia of a polymer chain. The ratio of coefficients of z is 1.91:1.33:1. This represents that the effect of excluded volume forces is very anisotropic; this effect has the tendency to strengthen further the asymmetrical distribution of segments in the unperturbed state.

It has been well known that the distribution of segments about the center of mass is not spherically symmetric but may be regarded as approximately ellipsoidal. The ratios of the principal orthogonal components of a ellipsoid are a quantitative measure of this asymmetrical distribution. Since the sum of three principal components equals the square radius of gyration S^2, the problem of determining the values of principal components equals that of decomposing the square radius of gyration S^2 into its three orthogonal components λ_i ($\lambda_1 \geq \lambda_2 \geq \lambda_3$) along the principal axis of inertia of the chain.

Many years ago Kuhn[1] drew attention to strong asymmetry of a random-flight chain following from consideration of average loci of several special segments in the chain relative to its end-to-end vector. A priori or a qualitative introduction of this asymmetrical distribution has played an important role in the theory of the excluded volume effect[2] and nonequilibrium properties of dilute polymer solutions such as viscosity and diffusion coefficient of flexible chains with and without the excluded volume effect.[3]

Recent works on the shape of a random-flight chain clearly reveal this asymmetry from quantitative points of view. In 1971 Šolc[4] showed, by the Monte Carlo method, that in the absence of the excluded volume effect, the intersegmental hydrodynamic interaction, and external perturbations (such as shear flow), a surprisingly high ratio of principal components is found to be

$$\lambda_1:\lambda_2:\lambda_3 = 12:2.7:1 \tag{1}$$

A little later Doi and Nakajima[5] proposed a method, as mentioned below, for a theoretical estimation of principal components, based on the spring bead model (Rouse model[6]), and showed that it reproduces fairly well the above high ratio.

It is expected, however, that owing to the presence of the

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