

# The Equation of State of a Polydimethylsiloxane Fluid

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## Synopsis

Experimental data for the dependence of the specific volume on temperature and pressure (PVT data) of a polydimethylsiloxane fluid with 100 cS viscosity are presented. The temperature range covered is 30–344°C and the pressure range is 0–200 MPa (0–29,000 psi). Coefficients for an empirical equation of state are reported. This equation of state is based on a polynomial fit to the zero-pressure isobar, combined with the Tait equation. The maximum deviation in specific volume between the data and the fitted empirical equation of state is less than 0.006 cm<sup>3</sup>/g, or less than 0.05% of the volume, except at the highest temperature, where sample degradation is likely to occur. The isothermal compressibility and thermal expansivity are derived from the empirical equation of state, and both show a strong temperature and pressure dependence. Reducing parameters for the Simha-Somcynsky theoretical equation of state were found to be  $P^* = 502$  MPa,  $V^* = 0.9765$  cm<sup>3</sup>/g, and  $T^* = 8175$  K. A comparison between theory and experimental data at temperatures to 245°C (recommended upper use temperature) revealed volume deviations comparable to those obtained using the Tait equation.

## INTRODUCTION

Polydimethylsiloxane fluids (PDMS) are characterized by good heat stability and lubricity. They are commonly used as heat transfer fluids, mold release agent, etc. For example, we use Dow-Corning 210H fluid as a pressurizing fluid in pressure–volume–temperature (PVT) experiments. In these experiments, hydrostatic pressure of 200 MPa (29,000 psi) and temperature up to 400°C (752°F) are reached (see below).

It is, of course, of very general engineering interest to characterize fluids with an equation of state that describes its thermophysical behavior accurately. PVT data of fluids can also be analyzed in terms of theoretical equations of state developed for polymeric fluids.<sup>1</sup> PDMS fluids permit the evaluation of such equations of state over a larger temperature range than most other polymer systems, which generally undergo a solidification in the accessible temperature range.

Many PVT measurements have been reported on polymer liquids and solids.<sup>1</sup> Work on PDMS fluids includes a report by Lichtenthaler et al.<sup>2</sup> on the effect of viscosity (3–1000 cP), on the specific volume at temperatures between 25 and 70°C and pressures to 900 bar. Beret and Prausnitz<sup>3</sup> reported PVT measurements for high molecular weight PDMS covering the same temperature range and pressures to 1000 bar. Dee and Walsh<sup>4</sup> reported reducing parameters

for PDMS for a number of theoretical equations of state, based on data covering pressures from 0 to 200 MPa and temperatures from 30 to 235°C.

## EXPERIMENTAL

### Sample

The PDMS fluid studied was Dow-Corning 210H fluid, with weight-average molecular weight believed to be about 5000 and viscosity of 100 cS at 25°C (information supplied by the manufacturer). It is also believed to contain heat stabilizers.

The sample was outgassed at 40°C for 48 h in a vacuum oven before testing. The density was then measured, using a Mettler/Par DM A40 density meter. We obtained 0.9655 g/cm<sup>3</sup> (specific volume = 1.0357 cm<sup>3</sup>/g) at 22°C.

### PVT Measurements

The apparatus used is a commercially available PVT apparatus,<sup>5</sup> based on the principles discussed previously.<sup>6</sup> The sample is contained in a rigid sample cell with a flexible bellows at one end. The volume not taken by the sample is filled with mercury under vacuum. The cell is placed inside a pressure vessel in which temperatures to 400°C and pressures to 200 MPa can be maintained. The deflection of the bellows as a result of temperature and/or pressure changes is measured by a linear variable differential transducer. The deflections are converted to volume changes of the sample itself by making known the PVT properties of the confining mercury. The accuracy of the apparatus is ±0.002 cm<sup>3</sup>/g to 250°C and 0.004 cm<sup>3</sup>/g at higher temperatures, with a sensitivity of better than 0.0005 cm<sup>3</sup>/g.

The mass of sample used in this experiment was about 1.5 g. The experiment was run in the isothermal mode. Starting at 30°C, the sample was compressed along 17 isotherms spaced 20°C apart, up to 344°C. Data were recorded along each isotherm from 10 to 200 MPa in 10 MPa intervals. Points reported for atmospheric (zero) pressure are extrapolated from higher pressures. Direct measurements at zero pressure are not attempted because of the possibility of gases (outgassing, degradation products) being trapped and affecting the results.

## RESULTS AND DISCUSSION

Figure 1 shows the general PVT relationship of PDMS as a selection of cross plotted isobars, spaced 40 MPa apart. A complete listing of the data is available from the authors. The specific volume at atmospheric pressure, except for the last isotherm, which is ignored throughout the analysis because of suspected degradation, was fitted to the following equation:

$$V(0, T) = A_1 + A_2T + A_3T^2 + A_4T^3 \quad (1)$$

For the volume expressed in cm<sup>3</sup>/g and temperature in °C, the values of the coefficients are

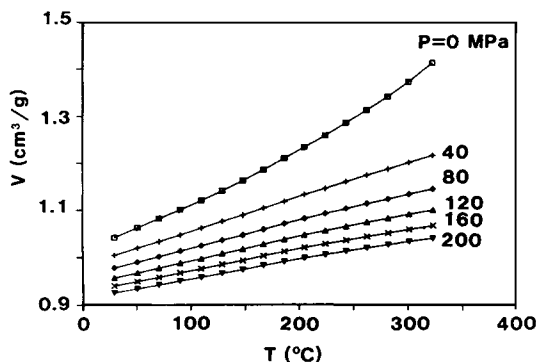


Fig. 1. Selected cross-plotted isobars in the PVT relationship of Dow-Corning PDMS 210H.

$$A_1 = 1.0158 \text{ cm}^3/\text{g}$$

$$A_2 = 8.91 \times 10^{-4} \text{ cm}^3 \text{ g}^{-1} \text{ }^\circ\text{C}^{-1}$$

$$A_3 = 5.19 \times 10^{-7} \text{ cm}^3 \text{ g}^{-1} \text{ }^\circ\text{C}^{-2}$$

$$A_4 = 1.48 \times 10^{-9} \text{ cm}^3 \text{ g}^{-1} \text{ }^\circ\text{C}^{-3}$$

Using these coefficients, eq. (1) represents the measured data to better than  $0.003 \text{ cm}^3/\text{g}$  over the whole temperature range.

A commonly used method of describing the specific volume as a function of pressure is based on the empirical Tait equation. This equation has been shown to represent accurately the volume of a large number of polymer glasses and melts.<sup>1</sup> It relates the volume  $V(P, T)$  at any pressure along an isotherm to the zero-pressure volume  $V(0, T)$  at the same temperature, in terms of two parameters  $C$  and  $B(T)$ :

$$V(P, T) = V(0, T) \{1 - C \ln[1 + P/B(T)]\} \quad (2)$$

The Tait parameter  $B(T)$  generally shows an exponential temperature dependence:

$$B(T) = B_1 \exp(-B_2 T) \quad (3)$$

PDMS is well described by the Tait equation, using the "standard" value of  $C = 0.0894$  in eq. (2). Values for  $B_1$  and  $B_2$  were determined by least-square fitting:

$$B_1 = 101 \text{ MPa}$$

$$B_2 = 6.59 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$$

Data in the temperature range  $30\text{--}323^\circ\text{C}$  and pressures to 200 MPa were used to derive these fitted parameters. Use of these coefficients, together with the values of  $V(0, T)$  given above, predicts the measured specific volumes in the

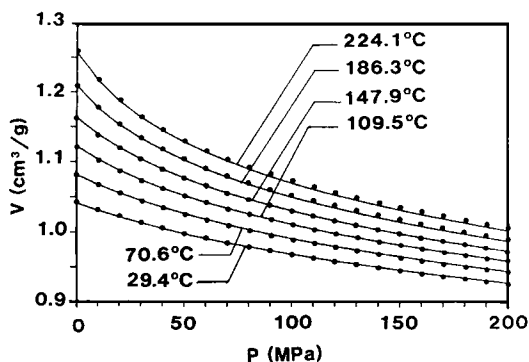


Fig. 2. Comparison between experimental data and Tait equation fits, using the parameters in the text.

whole measured range to better than 0.05%. This agreement is judged to be excellent, although some systematic deviations are apparent. These kinds of deviations are commonly found, and simply indicate that the Tait equation does not represent the equation of state in every detail. Figure 2 shows the measured volumes and the fits at selected temperatures.

Lichtenthaler et al. reported values for both coefficients  $B_1$  and  $B_2$ , derived from data in the limited temperature range 25–79°C and pressures to 900 bars (90 MPa) for PDMS fluids of different viscosities.<sup>2</sup> Comparing the values reported for their sample PDMS 100 (viscosity 100 cP, about the same as our sample) with our values, we found a difference of 9–12% in the Tait parameter, with our  $B$  values systematically higher (see Fig. 3). We believe our values are more representative of PDMS because of the larger temperature and pressure ranges used and because of the improved experimental technique. The specific volumes at zero pressure reported for PDMS 100 and the values predicted by eq. (1) are in excellent agreement, with our values systematically higher by 0.2%.

The Tait equation is particularly useful when calculating thermodynamic quantities such as the isothermal compressibility and the thermal expansivity. The isothermal compressibility,  $K = -1/V(dV/dP)_T$ , derived from eq. (2) is

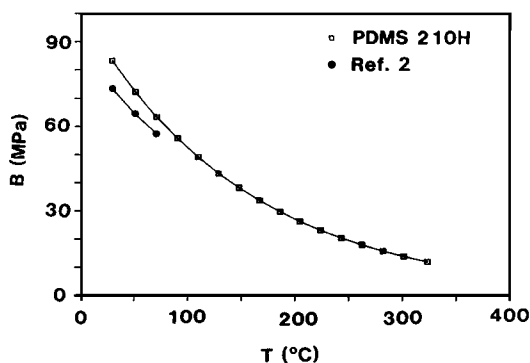


Fig. 3. Temperature dependence of the Tait parameter  $B(T)$ .

$$K(P, T) = ([P + B(T)]\{1/C - \ln[1 + P/B(T)]\})^{-1} \quad (4a)$$

In particular at  $P = 0$

$$K(0, T) = C/B(T) \quad (4b)$$

The Tait parameter is thus inversely proportional to the atmospheric-pressure compressibility and proportional to the bulk modulus at zero pressure (since the compressibility is the inverse of the bulk modulus). Figure 4 presents results for the compressibility calculated from eq. (4a), using the parameters given above. It shows that the compressibility increases with temperature and decreases with pressure, as expected. The atmospheric pressure compressibility changes by a factor of 8 over the whole temperature range, but this might in part be the result of some sample degradation at higher temperatures. This PDMS fluid is recommended for long term use at temperatures below 250°C only.

The thermal expansivity  $\alpha = 1/V(dV/dT)_P$  can also be derived from the Tait equation as

$$\alpha(P, T) = \alpha_0 - PB_2K(P, T) \quad (5)$$

in which  $\alpha_0 = 1/V(dV(0, T)/dT)_{P=0}$  is the zero-pressure thermal expansivity. It is derived from either eq. (1) or any other suitable expression for the volume at zero pressure. The thermal expansivity decreases with pressure according to eq. (5).

The equation of state of Simha and Somcynsky<sup>7</sup> has been shown to give an accurate representation of the equation of state for many polymers.<sup>4,8</sup> The theory and its application has been described fully in the literature and no attempt to discuss this theory is made here.<sup>7,9</sup> Suffice to say that the equation of state is in universal reduced form. A fit of experimental data to the theory consists of determining the reducing parameters  $P^*$ ,  $V^*$ , and  $T^*$  by which the reduced quantities of the theory are multiplied to obtain the actual quantities. The reducing parameters were determined using data between 30 and 243°C and

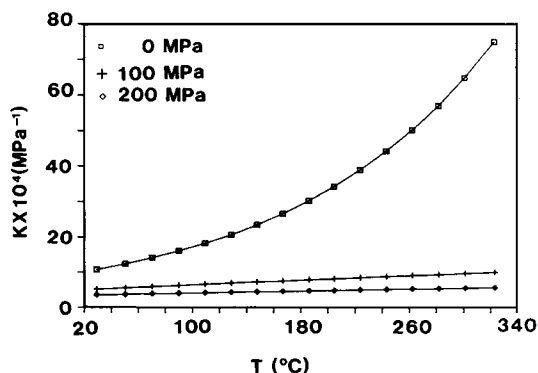


Fig. 4. Isothermal Compressibility calculated from the Tait equation.

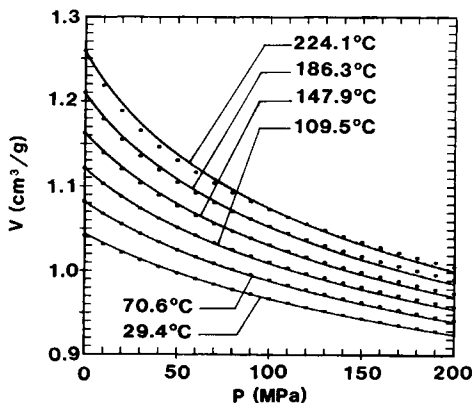


Fig. 5. Comparison between experimental data and Simha-Somcynsky theoretical fits, using  $P^* = 502$  MPa,  $V^* = 0.9765$  cm<sup>3</sup>/g, and  $T^* = 8175^\circ$ K.

pressures to 200 MPa. We found  $P^* = 502$  MPa,  $V^* = 0.9765$  cm<sup>3</sup>/g, and  $T^* = 8175$  K. The usual procedure was used, in which  $V^*$  and  $T^*$  were first determined from the zero-pressure isobar alone. For each pressure point, a reducing pressure was then determined to force exact agreement between theory and experiment. The values of  $P^*$  determined in this manner were then averaged. This average was accepted as the final value of  $P^*$ . The average extended over 240 points, and the standard deviation was 0.3%. The agreement between theory and data is similar to that found in other polymers,<sup>9</sup> and may be judged with respect to Figure 5. It may also be noted that the deviations found are of magnitude similar to those between the Tait equation and the experiment. As usual, better fits could be found by further decreasing the ranges of the data, suggesting that this theoretical equation is not a perfect fit. However, Dee and Walsh showed that the Simha-Somcynsky theory presented the best fit for PDMS when compared with other theoretical models.<sup>4</sup>

From the reducing parameters which contain the molecular characteristics of the polymer, the following relation can be derived:

$$M_0(P^*V^*/T^*) = R/3 \quad (6)$$

in which  $M_0$  is the molecular weight of a segment with exactly one external degree of freedom and  $R$  is the universal gas constant. Using the values obtained for the reducing parameters, we find  $M_0 = 46.2$ . This means that a PDMS chemical repeat unit, with a molecular weight of 74, has 1.6 external degrees of freedom. Comparing this value with the 0.8 degree of freedom for polyoxymethylene<sup>10</sup> and noting that the CH<sub>3</sub> groups did not seem to add external degrees of freedom when attached directly to backbone carbon atoms in a comparison of the PVT properties of polyethylene and polypropylene,<sup>11</sup> we conclude that the Si—O bond in the repeat unit of PDMS is more flexible than the C—O bond. This is an expected result, but may be taken as further confirmation of the basic soundness of the assumptions inherent in the Simha-Somcynsky theory.

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