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# Thermophysical Properties of Liquid Poly(methylsiloxane)s

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This paper report the density, viscosity, thermal conductivity, and heat capacity of 10 samples of poly(methylsiloxane) liquids (molecular mass from 298 to 14 887) at atmospheric pressure over the temperature range from 293 K to 493 K. The maximum relative measurement error is ±0.05%, ±2.4%, and ±0.8% for density, viscosity, and heat capacity, respectively.

## Introduction

The results of previous work on the investigation of the thermal conductivity of liquid poly(methylsiloxane)s was presented by Nemzer (1997). In this work the study of the density, viscosity, and heat capacity of 10 samples of poly(methylsiloxane) liquids (PMS) are reported over the range of temperatures from 293 K to 493 K. Poly(methylsiloxane) liquids are used in industry as dielectrics, heat carriers, lubricants, and oils. They are also used in hydraulics, damping apparatus installations, and diffusion pumps.

Poly(methylsiloxane) liquids are polymers with a linear structure. The molecules of PMS consist of large quantities of interchanging silicon and oxygen atoms where the free valences of silicon are replaced by methyl radicals.

The formula for these liquids has the following form

$$(CH_3)_3SiO[(CH_3)_2SiO]_n(CH_3)_3Si$$

where $n$ is the degree of polymerization.

## Experimental Section

The density in the temperature range (293−493) K at atmospheric pressure was measured using a special installation consisting of a hydrostatic balance described by Nemzer and Rastorguev (1969). The liquid under investigation was poured into a special purpose metallic thin-walled beaker set up in the thermostat whose temperature was maintained at the desired temperature with an accuracy of ±0.1 K.

The mass of the float was measured with an analytical balance with a resolution of ±0.1 mg. The float, made of glass and filled to $^2/_3$ of its volume with quartz sand, was suspended to the balance with a thin nichrome wire, 0.1 mm in diameter.

The liquid density was calculated by the equation

$$\rho_T = [(M - M')(1 - \rho_a/\rho_{wt}) - V_{wr}\,(\rho_T - \rho_a)]/V_T + \rho_a \quad (1)$$

where $M$ is the mass of the balance weights that counterbalance the float in the air, $M'$ is the mass of the weights counterbalancing the float in the fluid under study at temperature $T$, $\rho_a$ is the air density, $\rho_{wt}$ is the density of the weights material, $V_{wr}$ is the volume of the wire immersed in the liquid, and $V_T$ is the volume of the float.

The volume of the float at different temperatures was determined by calibration tests with distilled water and heptane (Rastorguev and Grigoryev, 1967). The maximum relative error of the density measurements using the method of hydrostatic weighing was estimated to be ±0.05%.

The kinematic viscosity $\nu$ was determined with a Pinkevich capillary viscosimeter (Rastorguev and Ganiev, 1967). For temperatures of up to 393 K, mineral oil was used as the thermostat liquid, and for higher temperatures, the organosilicon liquid PMS-100 was used. The viscosity measurement were made with viscosimeters with capillaries of 0.6, 0.8, 1.0, 1.2, and 1.5 mm diameter. The maximum relative error of the viscosity measurements was estimated to be ±2.4%.

The heat capacity was measured in the adiabatic calorimeter by the method of direct heating.

The calorimetric vessel was made of Pyrex glass, surrounded by a vacuum jacket, and had a volume of about 330 cm$^3$.

Control of the heat leak was accomplished by means of a differential three-junction chromel−copper thermocouple. The calorimetric vessel was placed into the water or PMS-100 liquid thermostat. The calorimeter constant was determined from measurements with water. At a temperature of 293 K, the calorimeter constant was 0.059 kJ K$^{-1}$. A detailed description of the experimental apparatus and the measurement method has been given by Rastorguev and Ganiev (1967).

## Results

In Table 1 the following are listed: density at 293 K, $\rho_0$; thermal expansion coefficient, $\alpha = (\partial\rho/\partial T)_p$; kinematic viscosity, $\nu_0$; dynamic viscosity, $\eta_0$; constant pressure heat capacity at 293 K, $C_{p0}$; temperature coefficient of heat capacity, $(\partial C/\partial T)_p$; molecular mass, $M$; mean degree of polymerization, $n$; number of atoms of silicon in the molecule, Si; refractive index at 293 K, $n_0^r$; thermal conductivity at 293 K, $\lambda$; and temperature coefficient of thermal conductivity, $(\partial\lambda/\partial T)_p$.

The experimental density data given in Table 2. Over the range of temperatures covered, the liquid density is described, with an deviation not exceeding the measurement error, by the following linear equation:

$$\rho_T = \rho_0[1 - \alpha(T - T_0)] \quad (2)$$

With increasing number of atoms of Si in the molecule, the density increases and tends to reach a limiting value

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**Table 1. Characteristics of the Poly(methylsiloxane) Liquids**

| | | | | | | constants | | |
|---|---|---|---|---|---|---|---|---|
| polymer | $\rho_0$/kg m$^{-3}$ | $10^2\alpha$/K$^{-1}$ | $n_0^r$ | $10^{-6}\nu_0$/m$^2$ s$^{-1}$ | $10^3\eta$/N s m$^{-2}$ | $A$ | $a$ | $k$ |
| PMS-1.5 | 852.1 | 0.116 | 1.3893 | 1.52 | 1.37 | 0.2541 | 50 | 1.2457 |
| PMS-5 | 912.7 | 0.099 | 1.3987 | 5.17 | 4.70 | $6.026 \times 10^5$ | 198 | 3.4675 |
| PMS-10 | 932.8 | 0.093 | 1.4018 | 9.84 | 9.18 | $5.248 \times 10^7$ | 208 | 4.1385 |
| PMS-50 | 957.4 | 0.088 | 1.4047 | 42.45 | 40.4 | $6.516 \times 10^{14}$ | 376 | 6.2388 |
| PMS-100 | 968.4 | 0.087 | 1.4047 | 107.98 | 104 | $2.328 \times 10^4$ | 91.5 | 2.6124 |
| PMS-200 | 970.2 | 0.087 | 1.4054 | 216.42 | 209 | $6.668 \times 10^7$ | 158 | 3.7785 |
| PMS-400 | 970.8 | 0.086 | 1.4059 | 395.51 | 383 | $9.954 \times 10^{15}$ | 330 | 6.4517 |
| PMS-476 | 972.5 | 0.086 | 1.4061 | 467.14 | 453 | $2.582 \times 10^8$ | 174 | 3.8272 |
| PMS−700 | 972.9 | 0.085 | 1.4049 | 698.17 | 677 | $1.409 \times 10^6$ | 120 | 2.9438 |
| PMS-1000 | 973.1 | 0.085 | 1.4058 | 1013.85 | 984 | $4.955 \times 10^8$ | 172 | 3.8109 |

| polymer | $C_{p0}$/kg J kg$^{-1}$ K$^{-1}$ | $10^2$ $(\partial C/\partial T)_p$/K$^{-1}$ | $M$/g mol$^{-1}$ | $n$ | Si | $\lambda_0$/W m$^{-1}$ K$^{-1}$ | $10^2(\partial\lambda/\partial T)_p$/K$^{-1}$ |
|---|---|---|---|---|---|---|---|
| PMS−1.5 | 1.586 | 0.212 | 298 | 2 | 4 | 0.107 | 0.126 |
| PMS−5 | 1.573 | 0.209 | 431 | 4 | 6 | 0.121 | 0.120 |
| PMS-10 | 1.547 | 0.205 | 739 | 8 | 10 | 0.136 | 0.118 |
| PMS−50 | 1.470 | 0.193 | 2975 | 38 | 40 | 0.153 | 0.113 |
| PMS−100 | 1.424 | 0.190 | 5011 | 66 | 68 | 0.159 | 0.110 |
| PMS−200 | 1.409 | 0.189 | 6675 | 88 | 90 | 0.162 | 0.111 |
| PMS−400 | 1.393 | 0.187 | 9634 | 128 | 130 | 0.163 | 0.106 |
| PMS−476 | 1.385 | 0.187 | 10189 | 136 | 138 | 0.164 | 0.110 |
| PMS−700 | 1.374 | 0.183 | 12336 | 164 | 166 | 0.165 | 0.107 |
| PMS−1000 | 1.363 | 0.178 | 14887 | 198 | 200 | 0.165 | 0.105 |

**Table 2. Densities, $\rho$/kg m$^{-3}$, of the Poly(methylsiloxane) Liquids**

| | $T$/K | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| polymer | 293 | 313 | 333 | 353 | 373 | 393 | 413 | 433 | 453 | 473 | 493 |
| PMS−1.5 | 852.1 | 832.8 | 809.6 | 790.9 | 769.7 | 753.6 | 731.7 | 712.0 | 691.3 | 672.6 | 653.4 |
| PMS−5 | 912.7 | 891.7 | 874.6 | 857.6 | 838.5 | 821.3 | 803.5 | 783.4 | 766.8 | 749.5 | 731.4 |
| PMS−10 | 932.8 | 919.3 | 902.9 | 886.3 | 867.1 | 852.5 | 833.1 | 816.7 | 796.4 | 780.7 | 763.7 |
| PMS−50 | 957.4 | 944.3 | 923.5 | 910.6 | 886.2 | 876.8 | 856.8 | 844.3 | 824.3 | 808.3 | 792.3 |
| PMS−100 | 968.4 | 953.6 | 932.6 | 918.9 | 899.1 | 888.3 | 863.8 | 856.6 | 833.6 | 818.2 | 803.9 |
| PMS−200 | 970.2 | 955.2 | 936.4 | 918.8 | 900.2 | 887.9 | 866.8 | 853.0 | 833.4 | 819.2 | 906.4 |
| PMS−400 | 970.8 | 956.1 | 936.5 | 923.9 | 903.8 | 890.1 | 870.5 | 856.8 | 836.1 | 823.5 | 809.9 |
| PMS−476 | 972.5 | 956.7 | 936.5 | 924.8 | 904.4 | 890.1 | 872.1 | 857.5 | 836.4 | 823.7 | 809.7 |
| PMS−700 | 972.9 | 958.4 | 937.2 | 925.4 | 905.3 | 892.3 | 872.7 | 858.2 | 838.2 | 826.4 | 814.6 |
| PMS−1000 | 973.1 | 957.7 | 937.2 | 925.4 | 905.9 | 892.4 | 871.8 | 838.4 | 835.2 | 826.3 | 814.8 |

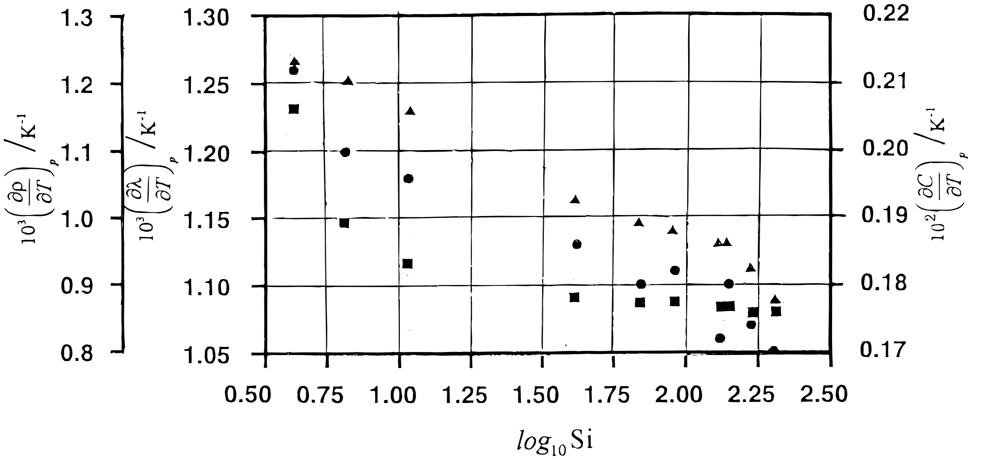

**Figure 1.** Temperature dependence of the coefficient, as a function of the number of Si atoms in the molecule: ■, $(\partial\rho/\partial T)_p$, ● $(\partial\lambda/\partial T)_p$; ▲, $(\partial C/\partial T)_p$.

(Figures 1 and 2). The coefficient of thermal expansion α decreases as does the temperature coefficient of the thermal conductivity (Nemzer, 1997). Here there is an analogy with the normal paraffin hydrocarbons, since they also have a linear structure, like PMS (Rastorguev and Ganiev, 1967; Rastorguev and Grigoryev, 1967).

With an increase of the degree of polymerization $n$ and the number of atoms of Si in the molecule, both the viscosity and temperature coefficient of viscosity increase.

As the Si number increases, the temperature coefficient of viscosity increases at first sharply, and then more slowly, tending to a limiting value. The temperature coefficient of viscosity $(\partial\nu/\partial T)_p$ varies for the liquids under consideration from 1.0 to 1.7.

The relatively weak dependence the viscosity of the poly(methylsiloxane) liquids on temperature as compared to oils permits their use as high-temperature lubricating oils and hydraulic liquids.

Among the numerous equations suggested for the description of the viscosity dependence of the temperature, the best description is the interpolation equation of Bachinski (1913)

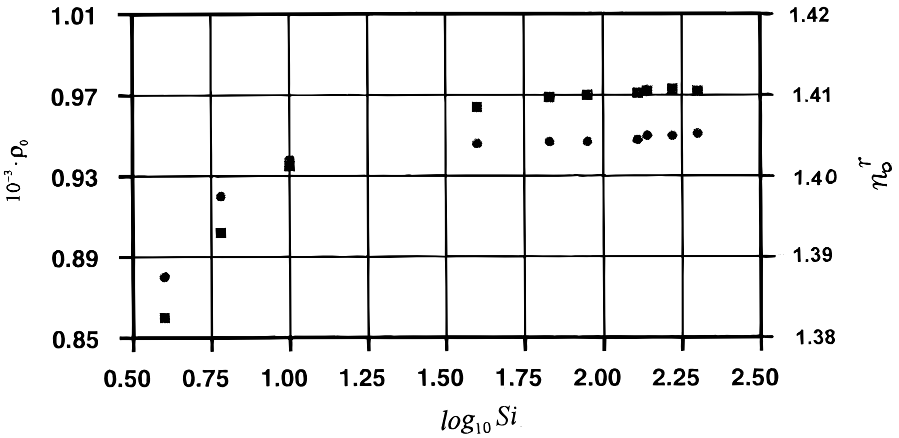

**Figure 2.** Dependence of $\rho_0$ and $n_0^r$ on the number of Si atoms in the molecule: ●, $n_0^r$; ■, $\rho_0$.

**Table 3. Viscosities, $10^3\eta$/N s m$^{-2}$, of the Poly(methylsiloxane) Liquids**

| | *T*/K | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| polymer | 293 | 313 | 333 | 353 | 373 | 393 | 413 | 433 | 453 | 473 | 493 |
| PMS−1.5 | 1.37 | 0.95 | 0.71 | 0.61 | 0.48 | 0.43 | 0.36 | 0.33 | 0.31 | 0.27 | 0.23 |
| PMS−5 | 4.70 | 3.54 | 2.20 | 2.07 | 1.55 | 1.30 | 1.01 | 0.86 | 0.68 | 0.59 | 0.48 |
| PMS−10 | 9.18 | 6.65 | 4.59 | 3.57 | 2.57 | 2.09 | 1.55 | 1.29 | 0.99 | 0.85 | 0.66 |
| PMS−50 | 40.4 | 30.4 | 21.6 | 17.2 | 12.5 | 10.2 | 7.57 | 6.27 | 4.75 | 3.99 | 3.09 |
| PMS−100 | 104 | 69.7 | 45.8 | 34.8 | 24.8 | 20.1 | 15.1 | 12.8 | 9.95 | 8.72 | 7.01 |
| PMS−200 | 209 | 143 | 95.3 | 71.8 | 50.3 | 39.8 | 29.1 | 24.1 | 18.1 | 15.3 | 11.9 |
| PMS−400 | 383 | 274 | 185 | 141 | 98.4 | 77.4 | 56.1 | 44.7 | 33.0 | 27.1 | 20.3 |
| PMS−476 | 453 | 319 | 215 | 166 | 117 | 94.50 | 69.9 | 58.2 | 44.3 | 37.8 | 30.1 |
| PMS−700 | 677 | 468 | 315 | 243 | 175 | 142 | 107 | 90.1 | 70.0 | 60.8 | 49.7 |
| PMS−1000 | 984 | 691 | 468 | 357 | 254 | 204 | 151 | 125 | 95.6 | 81.0 | 64.9 |

$$\eta = A/[(T - T_{273}) + a]^k \tag{3}$$

where *A*, *a*, and *k* are constants characteristic of the given liquid. Equation 3 conforms satisfactorily with the experimental data for the liquids considered here. The values of constants *A*, *a*, and *k* are given in Table 1. The calculations showed that the mean deviation of the experimental data (Table 3) from the values determined by eq 3 is +2.8%.

The viscosity results were compared with the theory of corresponding states. According to this theory, for a group of similar substances, the viscosity dependence on the temperature can be presented in the form of a universal function, the same for all the substances of the group, i.e.

$$\nu_T = \nu_\tau f(\tau) \tag{4}$$

where $\nu_\tau$ is the viscosity of the substance at the fixed value of the reduced temperature and $f(\tau)$ is the universal function for similar substances.

For PMS, as well as for petroleum compounds, it is convenient to define the reduced temperature through the temperature coefficient of density (Rastorguev et al., 1967)

$$\tau = \alpha_0 T \tag{5}$$

where $\alpha_0$ is the thermal expansivity, which is found using the formula

$$\alpha_0 = (\rho_1 - \rho_2)/(\rho_1 T_2 - \rho_2 T_1) \tag{6}$$

When calculating $\alpha_0$, one must remember that the accuracy of its determination depends on the selected temperature difference $\Delta T = T_1 - T_2$. The accuracy of determination of $\alpha_0$ increases as the temperature difference increases.

The experimental viscosity results in the temperature range (293−493) K are shown in the coordinates $\nu^* = \nu_T/\nu_{\tau=0.26}$, $\tau = \alpha_0 T$ (Figure 3). The figure shows that the experimental points fit rather well on the generalized curve whose equation can be written as follows

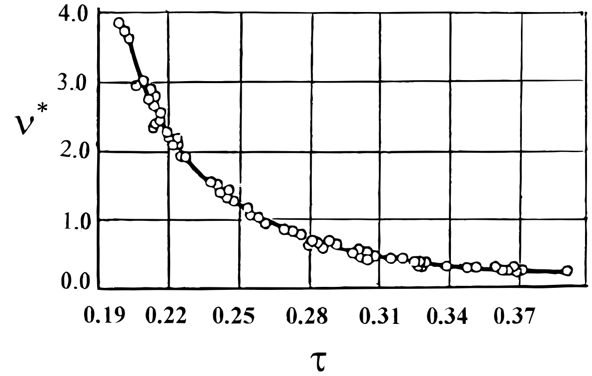

**Figure 3.** Dependence of $\nu^* = f(\tau)$ for all poly(methylsiloxane) liquids.

$$\nu^* = B/(\tau + b)^m \tag{7}$$

where $B = 4.46 \times 10^{-3}$, $b = -0.1007$, and $m = 2.938$.

The calculations demonstrate that the mean deviation of the experimental data from the values determined by eq 7 is 2.9%. Thus, eq 7 allows us to extrapolate from only one experimental value, with reasonably high accuracy, the PMS viscosity over rather a wide range of temperatures.

For all the liquids investigated, the heat capacity increases with temperature (Table 4) and over the measured range of temperatures it is described with an error of ±0.8% by the linear equation

$$C_{pT} = C_{p0}\,[1 + (\partial C/\partial T)_p(T - T_{293})] \tag{8}$$

where $C_{p0}$ is the heat capacity at 293 K and $(\partial C/\partial T)_p$ is the

**Table 4. Heat Capacities, $C_p$/kg J kg$^{-1}$ K$^{-1}$, of the Poly(methylsiloxane) Liquids**

| | *T*/K | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| polymer | 293 | 313 | 333 | 353 | 373 | 393 | 413 | 433 | 453 | 473 | 493 |
| PMS−1.5 | 1.584 | 1.653 | 1.716 | 1.792 | 1.857 | 1.928 | 1.984 | 2.061 | 2.118 | 2.195 | 2.254 |
| PMS−5 | 1.572 | 1.641 | 1.701 | 1.775 | 1.831 | 1.908 | 1.961 | 2.039 | 2.089 | 2.168 | 2.240 |
| PMS−10 | 1.548 | 1.612 | 1.671 | 1.742 | 1.794 | 1.869 | 1.922 | 1.997 | 2.510 | 2.123 | 2.194 |
| PMS−50 | 1.471 | 1.524 | 1.579 | 1.644 | 1.694 | 1.761 | 1.806 | 1.874 | 1.919 | 1.986 | 2.055 |
| PMS−100 | 1.423 | 1.476 | 1.529 | 1.591 | 1.636 | 1.699 | 1.743 | 1.809 | 1.852 | 1.917 | 1.983 |
| PMS−200 | 1.409 | 1.463 | 1.510 | 1.574 | 1.618 | 1.680 | 1.723 | 1.784 | 1.830 | 1.893 | 1.956 |
| PMS−200 | 1.409 | 1.463 | 1.510 | 1.574 | 1.618 | 1.680 | 1.723 | 1.784 | 1.830 | 1.893 | 1.956 |
| PMS−400 | 1.393 | 1.446 | 1.492 | 1.554 | 1.594 | 1.658 | 1.701 | 1.763 | 1.804 | 1.865 | 1.920 |
| PMS−476 | 1.385 | 1.439 | 1.482 | 1.546 | 1.589 | 1.651 | 1.692 | 1.752 | 1.795 | 1.856 | 1.916 |
| PMS−700 | 1.374 | 1.426 | 1.470 | 1.529 | 1.571 | 1.631 | 1.673 | 1.731 | 1.774 | 1.829 | 1.880 |
| PMS−1000 | 1.363 | 1.415 | 1.456 | 1.513 | 1.552 | 1.612 | 1.649 | 1.708 | 1.745 | 1.808 | 1.868 |

temperature coefficient of heat capacity. The values of $C_{p0}$ and $(\partial C/\partial T)_p$ for the PMS are given in the Table 1.

It follows from the analysis of the experimental data that as the degree of polymerization and the number of atoms of Si in the molecule increases, the heat capacity decreases, and its temperature coefficient also decreases (Figure 1).

To correlate the heat capacity $C_p$, we propose eq 9 below. This describes the temperature dependence of the heat capacity and relates $C_p$ to the density and molecular structure through the number of atoms of silicon in the molecules, Si.

$$C_p/\mathrm{J\ g^{-1}\ K^{-1}} = 1.405\left[1 + \left(\frac{T/\mathrm{K} + 223}{100}\right)(1.147 - 10^{-3}\ \rho/\mathrm{kg\ m^{-3}})\right] \times (1.21 + \mathrm{Si})/(0.86 + \mathrm{Si}) \quad (9)$$

Our calculation show that the average deviation of our experimental values of $C_p$ from 9 does not exceed 1.1%, with a maximum deviation of 2.6%.

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