Thermal Conductivity of Poly(ethylsiloxane) Liquids at High Pressures

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This paper describes an apparatus for the measurement of thermal conductivity at pressure and reports the thermal conductivity of poly(ethylsiloxane) liquids at high pressures. The experimental results are presented on the thermal conductivities of three poly(ethylsiloxane) liquids at pressures up to 200 MPa in the temperature range 293 K to 473 K. The maximum relative error of measurement is ±1.6%. Equations are given which fix the results over the temperature and pressure ranges studied.

Introduction

Poly(ethylsiloxane) liquids (PES) are used in various branches of industry such as dielectrics, heat carriers, lubricants, and oils. They are used for hydraulic, damping, and apparatus installations and for vacuum and diffusion pumps.

The poly(ethylsiloxane) liquids are polymers with linear structures. The molecules of PES consist of large quantities of interchanging silicon and oxygen atoms, and free valences of silicon are replaced by ethyl radicals. The formula of these liquids has the following form $(C_2H_5)_3SiO-[Si(C_2H_5)_2O]nSi(C_2H_5)_3$, where n is the degree of polymerization.

PES are transparent liquids, have no smell, are soluble in aromatic hydrocarbons and ethers, and are not soluble in water. Their characteristics make them highly compatible with mineral oils.

Experimental Section

The thermal conductivity was measured using a cell containing a coaxial cylinder with flat faces.

The general view of the measuring unit and high-pressure autoclave is given in Figure 1. The inner cylinder of the measuring unit has a diameter of (19.970 ± 0.001) mm, and the length of the cylindrical part is (200 ± 0.005) mm. Along the axis of the inner cylinder an orifice with a diameter of 6 mm is drilled to hold an electric heater. The heater is made of nichrome wire with a diameter of 0.15 mm and is contained within a stainless steel cover. To the end of the heater are soldered, with silver solder, the current-carrying copper wires with a diameter of 0.23 mm. The outside cylinder has an outside diameter of 35 mm and an inner diameter of (20.450 ± 0.01) mm. The inner cylinder was centered in the outside one with six porcelain strut sleeves with a diameter of 1.5 mm and with two removable centered bushings.

The porcelain strut sleeves were fixed by micrometric screws. The clearance at the ends of the cylinders was provided by textolyte strut sleeves, three from every (total six) side. Strut sleeves were placed on the end covers of the outside cylinder.

The inner and outer cylinders and end covers were made from refined copper. Their working surfaces were thoroughly ground, chromium plated, and polished. For mea-
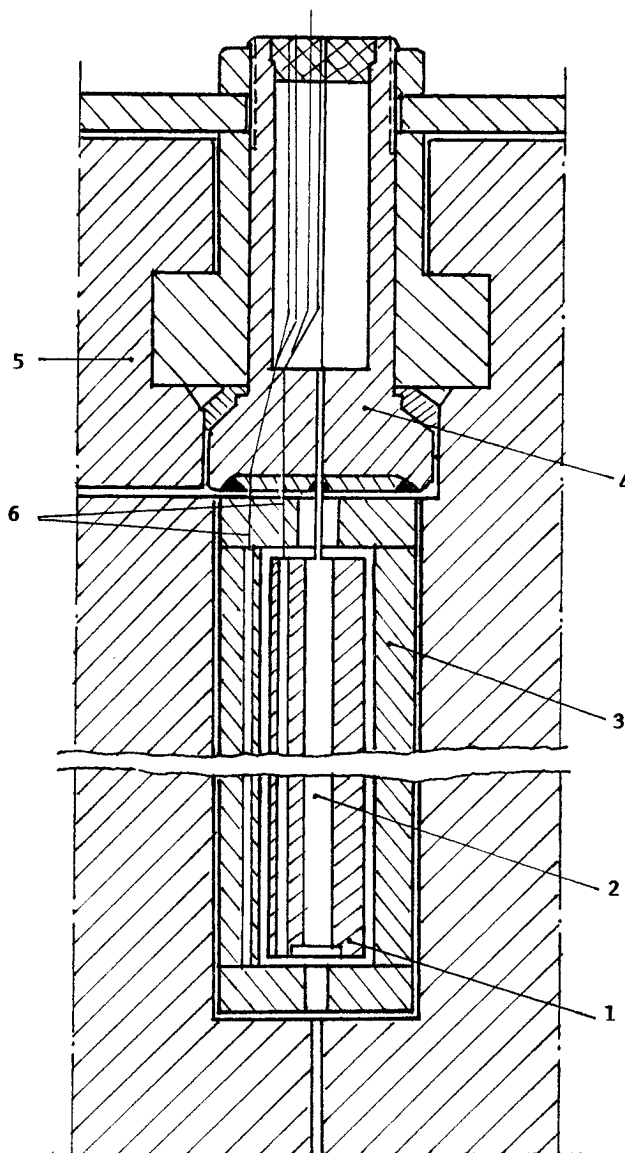
Figure 1. General view of the measuring unit and high-pressure autoclave: (1) inner cylinder; (2) electric heater; (3) outside cylinder; (4) compressing cylinder; (5) autoclave; (6) thermocouples.

suring the absolute temperature in the experiment and the temperature difference in the layer of the investigating

† Deceased.

Table 1. Characteristics of the Poly(ethylsiloxane) Liquids: Density, ρ_0; Viscosity, ν_0; Refractive Index, n_0^r; Molecular Mass, *M*; Mean Degree of Polymerization, *n*; Number of Atoms of Silicon in the Molecules, Si

polymer	ρ_0/kg·m^{-3}	n_0^r	$10^6\nu_0$/m^2·s^{-1}	M/g·mol^{-1}	n	Si	λ_{T_0}/W·m^{-1}·K^{-1}	10^2C	B
PES-2	913.40	1.4398	10.80	392.00	2	4	0.133	3.12	102.46
PES-4	957.80	1.4425	51.52	626.00	4	6	0.142	2.81	118.72
PES-5	991.00	1.4468	268.8	1607.00	14	16	0.157	2.64	120.87

Table 2. Thermal Conductivity λ (W·m^{-1}·K^{-1}) of the Poly(ethylsiloxane) Liquids as a Function of Pressure *P* and Temperature *T*

	P/MPa										
T/K	0.098	20	40	60	80	100	120	140	160	180	200
					PES-2						
297.1	0.1325	0.1391	0.1445	0.1491	0.1524	0.1551	0.1587	0.1613	0.1626	0.1642	0.1651
322.8	0.1289	0.1364	0.1422	0.1476	0.1511	0.1548	0.1579	0.1612	0.1624	0.1639	0.1651
354.3	0.1247	0.1323	0.1402	0.1451	0.1494	0.1541	0.1576	0.1608	0.1623	0.1634	0.1651
378.5	0.1211	0.1304	0.1374	0.1436	0.1488	0.1536	0.1576	0.1594	0.1616	0.1641	0.1651
410.3	0.1166	0.1278	0.1346	0.1423	0.1472	0.1528	0.1569	0.1591	0.1611	0.1632	0.1652
444.1	0.1123	0.1231	0.1311	0.1389	0.1462	0.1518	0.1562	0.1589	0.1611	0.1628	0.1652
467.7	0.1111	0.1206	0.1289	0.1369	0.1445	0.1511	0.1562	0.1589	0.1611	0.1631	0.1652
					PES-4						
301.4	0.1411	0.1463	0.1503	0.1534	0.1572	0.1592	0.1617	0.1634	0.1651	0.1668	0.1686
333.5	0.1362	0.1413	0.1469	0.1513	0.1551	0.1574	0.1613	0.1637	0.1651	0.1667	0.1684
364.4	0.1317	0.1387	0.1439	0.1492	0.1524	0.1571	0.1604	0.1632	0.1648	0.1666	0.1684
392.7	0.1284	0.1352	0.1417	0.1463	0.1511	0.1557	0.1601	0.1626	0.1643	0.1666	0.1682
402.9	0.1273	0.1342	0.1407	0.1453	0.1507	0.1554	0.1601	0.1627	0.1647	0.1665	0.1682
441.1	0.1213	0.1304	0.1367	0.1434	0.1493	0.1542	0.1591	0.1623	0.1639	0.1662	0.1682
471.3	0.1178	0.1178	0.1339	0.1415	0.1473	0.1536	0.1581	0.1611	0.1639	0.1662	0.1682
					PES-5						
304.2	0.1551	0.1601	0.1637	0.1681	0.1703	0.1734	0.1751	0.1783	0.1798	0.1818	0.1822
324.7	0.1521	0.1574	0.1619	0.1663	0.1682	0.1721	0.1741	0.1764	0.1784	0.1804	0.1821
362.8	0.1462	0.1534	0.1569	0.1624	0.1663	0.1701	0.1737	0.1761	0.1779	0.1801	0.1818
387.7	0.1425	0.1498	0.1549	0.1603	0.1648	0.1689	0.1719	0.1754	0.1771	0.1793	0.1814
404.6	0.1402	0.1469	0.1538	0.1587	0.1642	0.1679	0.1717	0.1751	0.1769	0.1793	0.1811
440.4	0.1349	0.1431	0.1498	0.1562	0.1616	0.1663	0.1708	0.1741	0.1765	0.1791	0.1806
469.8	0.1303	0.1391	0.1465	0.1539	0.1595	0.1651	0.1693	0.1732	0.1761	0.1787	0.1803

liquid, the nichrome−constantan thermocouples were placed in the inner and outer cylinders. The thermocouples were placed in two special covers made from stainless steel tubes. From the high-pressure zone the thermocouples were sealed with thin-sided metal capillaries, which were soldered into the thermocouple covers. The absolute and differential thermocouples were calibrated on a special stand with an exemplary resistance thermometer and a Beckman thermometer.

The high-pressure autoclave is made from stainless steel. The packing of the autoclave is made of stainless steel using a bayonet block.

The measuring unit in the autoclave was hung on three thin-sided metal capillaries, through which the current and thermocouple wires were led out. These capillaries were soldered into a steel disk, which was fixed to the compressing cylinder. The clearance between the measuring unit and the autoclave along the entire perimeter was a constant 0.4 mm.

During the experiments, the autoclave together with the measuring unit was placed into the thermostat with a volume of 0.12 m^3. A dry spindle oil was used as the thermostat liquid. The temperature in the thermostat was held constant to an accuracy of ±0.01 K with a special thermocontrol. The power supply of the electric heater of the measuring unit was a bank of accumulators. The current in the heater circuit was determined from the voltage across the standard resistor of class 0.01%. The voltages across the standard resistor, the electric heater, and the absolute and differential thermocouples were measured by potentiometers. The error in temperature difference measurement on the layer of the investigating liquid was estimated to be ±0.006 K. In order to exclude the influence of stray voltages all measurements were made with the current in both directions.

The measuring unit was filled with liquid under vacuum. The residual pressure in the system did not exceed 1.33 Pa. The pressure in the autoclave was created by a hydraulic press through a syphon separating vessel and was measuring by a load-piston manometer of class 0.05%.

The thermal conductivity of PES was calculated from the equation:

$$\lambda = \frac{I(U - \Delta U) - \sum Q_0}{\left(\dfrac{2\pi L}{\ln \dfrac{d_2}{d_1}} + \dfrac{2F}{\delta}\right)(\Delta t_{\mathrm{m}} - t)} \tag{1}$$

where *I* is the current in the heater circuit, *U* is the voltage across the heater, ΔU is the correction for the voltage on the copper current lead wires, $\sum Q_0$ is the correction for the loss of heat from the inner cylinder, Δt_{m} is the measured temperature difference in the layer, Δt is the correction for the thermocouple set, *L* is the length of the inner cylinder, d_2 is the inside diameter of the outer cylinder, d_1 is the outside diameter of the inner cylinder, δ is the thickness of the liquid layer, and *F* is the surface area of the end of the inner cylinder.

During the measurement of the thermal conductivity, particularly by absolute methods, strict attention should be given to the accuracy of the determination of the dimensions of the measuring unit.

The geometric constant was defined by measuring the electrical capacitance of the measuring unit. This method is well-known and gives the capability to determine the geometric constant with a high degree of accuracy (Leidenfrost, 1964). For the determination of the electrical capacitance we used the bridge for LCR measuring. The
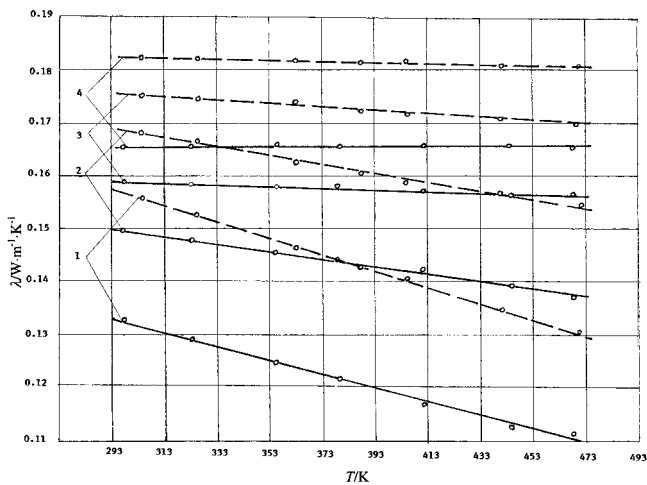
Figure 2. Dependence of the thermal conductivity on temperature: (—) for PES-2; (---) for PES-5; (1) 0.098 MPa; (2) 60 MPa; (3) 120 MPa; (4) 200 MPa.
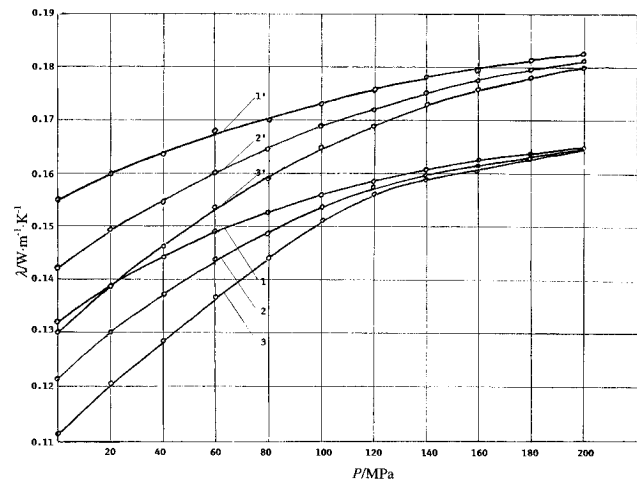
Figure 3. Dependence of the thermal conductivity on pressure. For PES-2: (1) 297.1 K; (2) 378.5 K; (3) 467.7 K. For PES-5: (1′) 304.2 K; (2′) 387.7 K; (3′) 471.8 K.

Figure 4. Dependence of the thermal conductivity on temperature and pressure for PES-2. For isobar: (1) 0.098 MPa; (2) 40 MPa; (3) 80 MPa; (4) 120 MPa; (5) 160 MPa; (6) 200 MPa. For isoterm: (1′) 297.1 K; (2′) 354.3 K; (3′) 410.3 K; (4′) 467.7 K.

error of the measurement was ±1 pF. The measurements were made at the constant temperature of 293 K, an atmospheric pressure of 0.101 MPa, and 60% relative humidity of the air.

The capacitance of the measuring unit at the strict coaxiality of the cylinders was (513 ± 1) pF, and the geometrical constant was $A_0 = 57.914$ m. At the temperature 473 K the correction for the change of the geometrical dimensions of the measuring unit was 0.34%. The correction for the voltage on the current lead wires ΔU in the experiment did not exceed 0.2%, and on the thermocouple set 0.4%.
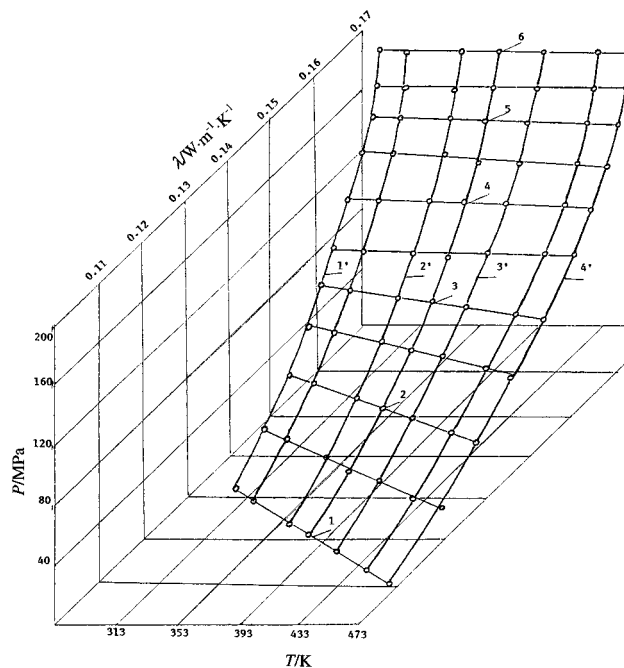
The correction for the heat loss from the inner cylinder is calculated from the correction for heat loss on the lead current wires, thermoelectrodes of the thermocouples, centralizing strut sleeves, and thin-sided metal capillaries.

The maximum relative error of measurement the thermal conductivity reached was ±1.6%.

Results of Measurements

Previous measurements (Nemzer and Rastorguev, 1969, 1970, 1975) on the thermal properties of poly(ethylsiloxane) liquids were made at atmospheric pressure.

In the present work, the thermal conductivity of PES-2, PES-4, and PES-5 are made at pressures up to 200 MPa and in a range of temperature of (293 to 473) K.

In Table 1 the following are listed: density at 293 K, ρ_0; viscosity at 293 K, ν_0; refractive index at 293 K, n_0^r; molecular mass, M; the mean degree of polymerization, n; and the number of atoms of silicon in the molecules, Si.

The thermal conductivity was measured isothermally through 20 MPa. Table 2 lists the effective thermal conductivity, which varies smoothly with pressure.

The analysis of experimental data shows that, as expected, the thermal conductivity of poly(ethylsiloxane) increases with increasing pressure and increases more rapidly at the highest temperatures.

At 293 K and an increase of pressure from 0.098 to 200 MPa, the thermal conductivity of PES-2, PES-4, and PES-5 increases by 22, 19, and 16%, respectively, and at 473 K by 55, 45, and 40%, respectively (Table 2).

For all fluids the isobars are approximately linear in pressure (Figures 2 and 4) but the isotherms show rather large curvature (Figures 3 and 4). With increasing temperature the curvature increases.

The results were fitted to the following equations:

$$\lambda_{PT} = \lambda_{T_0P} - \left(\frac{\partial\lambda}{\partial T}\right)_P^{mid}(T - T_0) \qquad (2)$$

where λ_{T_0P} is thermal conductivity at pressure and temperature $T_0 = 293$ K, and

$$\lambda_{T_0P} = \lambda_{T_0} + C\ln\left(1 + \frac{P}{B}\right) \qquad (3)$$

where λ_{T_0} is the thermal conductivity at atmospheric pressure and temperature $T_0 = 293$ K. The values of λ_{T_0} and constants C and B are listed in Table 1.

The dependence $(\partial\lambda/\partial T)_P^{mid}$ on pressure is described accordingly for PES-2, PES-4, and PES-5 by the following equations:

PES-2: $\quad (\partial\lambda/\partial T)_P^{mid}/\text{W·m}^{-1}\text{·K}^{-2} = 0.358 \times$
$10^{-8}(P/\text{MPa})^2 - 0.139 \times 10^{-5}(P/\text{MPa}) + 0.134 \times 10^{-3}$

PES-4: $\quad (\partial\lambda/\partial T)_P^{\text{mid}}/\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2} = 0.324 \times$
$10^{-8}(P/\text{MPa})^2 - 0.134 \times 10^{-5}(P/\text{MPa}) + 0.139 \times 10^{-3}$

$$(4)$$

PES-5: $\quad (\partial\lambda/\partial T)_P^{\text{mid}}/\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2} = 0.287 \times$
$10^{-8}(P/\text{MPa})^2 - 0.129 \times 10^{-5}(P/\text{MPa}) + 0.151 \times 10^{-3}$

The deviation of experimental data as calculated by (2) does not exceed the error of experiment.

Literature Cited

Leidenfrost, W. *Int. J. Heat Mass Transfer* **1964**, *7*, 27−31.
Nemzer, V.; Rastorguev, Y. *J. Plastic Mass* **1969**, *7*, 28−30.
Nemzer, V.; Rastorguev, Y. *J. Plastic Mass* **1970**, *8*, 14−16.
Nemzer, V.; Rastorguev, Y. *J. Oil Gas* **1975**, *6*, 55−59.