International Journal of Thermophysics, Vol. 6, No. 5, 1985

Ultrasonic Speeds and Densities of Poly(dimethylsiloxane) (Viscosity Grades 30 and $50 \times 10^{-4}\,\mathrm{m \cdot s^{-1}}$) at 298.15, 303.15, and 308.15 K Under High Pressures

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Received May 20, 1985

The ultrasonic speeds and densities of poly(dimethylsiloxane), viscosity grades 30 and $50 \times 10^{-4}\,\mathrm{m \cdot s^{-1}}$ at 298.15 K, were measured at 298.15, 303.15, and 308.15 K. The measurements were carried out using new apparatuses, one for measurement of the speed under pressures up to 200 MPa and another for measurement of the density under pressures up to 100 MPa. The former is constructed with a sing-around technique of the fixed-path type operated at a frequency of 2 MHz, and the latter is a dynamic bellows piezometer. The probable uncertainty in the present results is within ±0.23% for speed and ±0.19% for density for all the experimental conditions. The ultrasonic speed in these fluids at first increases rapidly with pressure and then indicates a mild rise in the high-pressure region. Similar pressure effects are observed for the density. The relationship between the speed and the density satisfied a first-order function well. The isentropic compressibility, derived from the speed and density, also showed a large pressure effect. The values and its pressure effects seemed almost independent of the viscosity of poly(dimethylsiloxane).

KEY WORDS: bellows piezometer; density; high pressure; poly(dimethylsiloxane); sing-around technique; ultrasonic speed.

1. INTRODUCTION

Poly(dimethylsiloxane) (PDMS) is usually used as a heat transfer medium or lubricant, since the fluid has several unique properties such as chemical stability, a moderate viscosity at high and low temperatures, and a low vapor pressure. Recently, investigations of low-temperature chemistry [1]

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and photochemistry [2] at high pressures are flourishing. In these works several PDMS, which do not freeze at low temperatures and high pressures, are used as the pressure transmitting medium. For these studies, the precise thermophysical properties of these fluids are needed; however, the properties under high pressure have not been investigated sufficiently.

The authors previously reported the ultrasonic speed in various pure organic liquids and binary mixtures measured under high pressure using a pulse technique [3–6]. Recently, we have constructed a new high-pressure apparatus for the measurement of ultrasonic speed with a sing-around technique of the variable-path type and observed the speeds in benzene and toluene under high pressure [7]. In general, a highly accurate value of the speed can be obtained by a sing-around technique at atmospheric pressure [8], but under high pressure the measuring process becomes extremely troublesome. We have improved the apparatus for more convenient and accurate measurement. In this paper, we report on the ultrasonic speeds in poly(dimetheylsiloxane), viscosity grades 30 and $50 \times 10^{-4}\,\mathrm{m \cdot s^{-1}}$ at 298.15 K (PDMS-30, PDMS-50), which were measured at temperatures of 298.15, 303.15, and 308.15 K under pressures up to 200 MPa. The densities for these fluids were also measured using a newly constructed apparatus employing a dynamic bellows piezometer at the same temperatures under pressures up to 100 MPa. The pressure effects on ultrasonic speed and density are discussed for PDMS. Our data for water, toluene, and *n*-octane are compared with data reported elsewhere.

2. EXPERIMENTAL

2.1. Materials

Benzene, toluene (spectral grade), and *n*-octane (reagent grade) used in the preliminary work were supplied by Dojin Chemical Co. or Nakarai Chemical Co. Eeach purity was better than 99.8% by volume. Poly(dimetheylsiloxane) contributed by Shinetsu Chemical Co. (Shinetsu Silicone Oil KF-96) was used without further purification. The refractive indices observed with an Abbe refractometer are 1.4013 for PDMS-30 and 1.4021 for PDMS-50 at 298.15 K. The densities of the materials at atmospheric pressure were memasured with an Ostwald pycnometer (about $20\,\mathrm{cm}^3$), and the results at each temperature are listed in Table II.

2.2. Ultrasonic-Speed Measurement

The method used for the measurement of ultrasonic speed was a sing-around technique: Cho-onpa Ind. Co. UVM-2, fixed-path type, with a

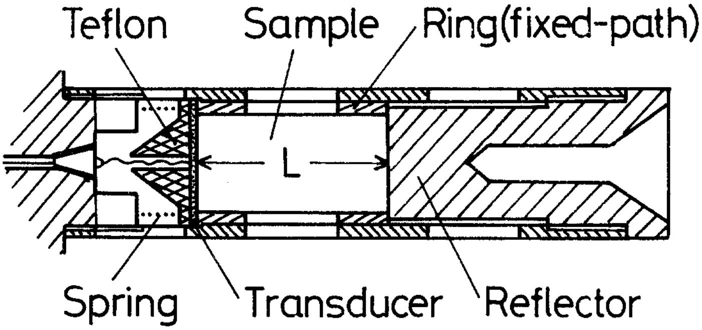

Fig. 1. Fixed-path interferometer ($L = 31.351$ mm).

single transducer employing a gated amplifier. Figure 1 shows the fixed-path interferometer. The pulsed ultrasonic wave, excited by the transducer (lead zincontitanate PZT, 20 mm in diameter, 2.0 MHz), was propagated in the sample. When the wave returned from the reflector to the transducer, the gate was opened electrically and the reflcted signal was detected by the same transducer. In this work, a delay line was employed to avoid the interference of multiple echoes. The next accoustic short pulse was generated a definite time (delay time $\tau = 511.272 \pm 0.0016\ \mu s$) after the arrival of the reflected wave. The ultrasonic speed u was obtained obtained from the average value of 1000 periods t including the delay time τ as follows,

$$u = 2L/(t - \tau) \tag{1}$$

where L is the distance between the transducer and the reflector, and this value (31.351 ± 0.0016 mm) was obtained from measured periods in benzene [8, 9] and toluene [7] at atmospheric pressure where the precise speeds are known. The interferometer was placed in a high-pressure vessel (stainless-steel SUS 420), which was immersed in a water bath controlled to within ±0.03 K during the experiment. The temperature was measured by a thermocouple of the T type calibrated with a standard thermometer. The pressure applied to the sample in the vessel was generated by means of a hand oil pump and transmitted through mercury. Under each experimental condition, the pressure was measured with a precise Heise bourdon gauge (16 in. in diameter, scaled at every 0.5 MPa up to 400 MPa), which was calibrated with a deadweight tester, and was accurate within ±0.3 MPa up to 200 MPa.

2.3. Density Measurement

The density was measured using a dynamic bellows piezometer made of stainless steel (SUS 304) as shown in Fig. 2. The piezometer was

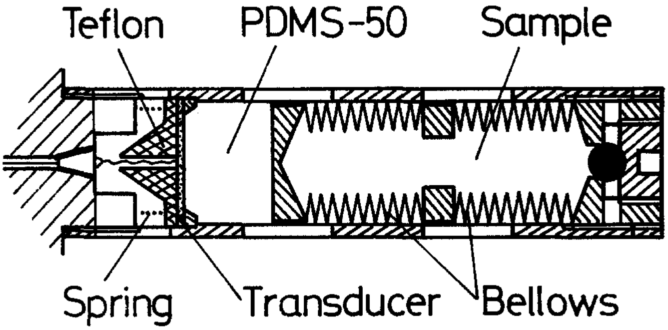

Fig. 2. Dynamic bellows piezometer (sample volume, about 5.6 cm^3).

calibrated with a mercury weight method. The calibration coefficient K (= volume/length) was $0.13332\ \mathrm{cm}^3 \cdot \mathrm{mm}^{-1}$. In conventional measurements of pVT using bellows piezometers, the bellows movement ΔL with pressure is estimated using electrical resistance [10] or a linear transformer [11]. In our work, we found that the value of ΔL can be obtained from the u and t values using Eq. (1). Thus, PDMS-50 was used as a pressure transmitting medium. The ΔL value accompanying the rise in pressure was derived by measuring the period of wave propagating between the transducer and the end of the bellows, $t_{(\mathrm{PDMS\text{-}50})}$, and the speed $u_{(\mathrm{PDMS\text{-}50})}$ obtained above, using the following equation:

$$\Delta L = L_0 - \{u_{(\mathrm{PDMS\text{-}50})}[t_{(\mathrm{PDMS\text{-}50})} - \tau]/2\} \tag{2}$$

The volume change ΔV of the sample in the piezometer with pressure can be calculated by

$$\Delta V = V_0 - K\Delta L \tag{3}$$

where L_0 and V_0 are the distance between the transducer and the end of the bellows and the sample volume at atmospheric pressure, respectively. The apparatus, except the piezometer, was identical to that used for the measurement of ultrasonic speed.

3. RESULTS AND DISCUSSION

As preliminary work, the ultrasonic speeds u in benzene were measured at 298.15 and 303.15 K under different pressures. The results are in good agreement with the values obtained by Bobic [9] using a pulse-echo method. In order to check the reliability of the present values at pressures higher than for benzene, the freezing pressure 907 MPa at

303.15 K [12], the ultrasonic speeds in toluene were also measured under pressures up to 200 MPa. The results are listed in Table I together with the values measured with a variable-path interferometer [7]. As can be seen clearly in Table I, the new values agree closely with the values reported in our previous paper (within ±2.0 m · s^{-1}) for the higher-pressure region.

Next, the densities ρ of *n*-octane were measured at 298.15 and 303.15 K under pressures up to 160 MPa. The results are listed in Table I. Benson and Winnick [10] measured the *pVT* properties of *n*-octane at several temperatures and pressures using a siphon-bellows piezometer. The densities derived from the Tait parameters reported in their paper are also listed in Table I. These values are in close agreement with the present results, within ±0.15%.

In the measurements of u and ρ in this work, the values observed under each condition showed a good reproducibility on repeated runs. The probable uncertainty is estimated, taking into account the errors in the measurement of temperature and pressure, to be less than 0.23% for u and ±0.19% for ρ over the whole range of the experiments.

Table I. Comparison of the Observed Ultrasonic Speed u in Toluene and the Density ρ for *n*-Octane with Literature Values[a]

p (MPa)	298.15 K		303.15 K	
	u (m · s^{-1}) in toluene			
	u_T	u_L	u_T	u_L
0.1	1310.6	1310.0	1288.3	1286.9
40	1486.5	1482.2	1467.3	1462.9
80	1624.7	1623.7	1608.9	1607.4
120	1740.7	1740.1	1725.4	1723.5
160	1842.7	1838.0	1826.5	1824.1
	ρ (kg · m^{-3}) for *n*-octane			
	ρ_T	ρ_L	ρ_T	ρ_L
0.1	698.4	698.1	694.1	694.0
30	721.5	720.5	716.8	717.0
60	738.6	738.0	734.5	734.7
90	753.3	752.4	749.4	749.4

[a] u_T and ρ_T, this work; u_L, Ref. 7; ρ_L, Ref. 10.

Table II. Experimental Values of Ultrasonic Speed u and Density ρ for PDMS-30 and PDMS-50[a]

p (MPa)	u ($\mathrm{m \cdot s^{-1}}$)	ρ ($\mathrm{kg \cdot m^{-3}}$)	p (MPa)	u ($\mathrm{m \cdot s^{-1}}$)	ρ ($\mathrm{kg \cdot m^{-3}}$)
PDMS-30					
298.145 K					
0.1	1000.1	953.4	90	1383.7	1024.7
5	1031.5	959.9	100	1415.0	1030.3
10	1060.9	965.4	110	1444.5	1035.9
15	1087.1	970.0	120	1472.7	1041.1
20	1112.5	974.7	130	1499.9	1046.1
25	1136.6	979.0	140	1526.3	1051.0
30	1159.6	983.1	150	1551.8	1055.7
40	1203.7	991.3	160	1574.8	1059.9
50	1244.5	998.1	170	1599.5	1064.5
60	1281.4	1005.7	180	1621.9	1068.6
70	1318.1	1012.6	190	1644.5	1072.8
80	1352.1	1018.8	200	1665.9	1076.7
303.15 K					
0.1	987.1	948.4	90	1374.6	1019.6
5	1018.3	953.8	100	1406.3	1025.1
10	1047.4	958.8	110	1435.7	1030.8
15	1076.3	964.7	120	1464.1	1036.1
20	1100.5	968.6	130	1491.5	1041.1
25	1125.6	973.4	140	1516.8	1045.8
30	1148.8	977.7	150	1543.3	1050.7
40	1193.1	985.9	160	1568.3	1055.3
50	1234.3	993.6	170	1591.6	1059.6
60	1272.4	1001.0	180	1614.9	1063.9
70	1308.7	1007.8	190	1638.1	1068.2
80	1353.5	1013.9	200	1659.5	1072.1
308.15 K					
0.1	972.6	944.0	90	1365.9	1015.7
5	1006.0	949.0	100	1396.8	1021.1
10	1036.2	954.2	110	1426.6	1025.3
15	1062.9	959.3	120	1455.1	1030.6
20	1089.0	964.2	130	1482.8	1035.7
25	1114.4	968.8	140	1508.5	1040.5
30	1137.7	973.4	150	1533.7	1045.1
40	1182.3	981.8	160	1559.2	1049.8
50	1223.8	989.6	170	1584.0	1054.4
60	1262.5	997.0	180	1606.1	1058.5
70	1298.9	1003.8	190	1629.7	1062.9
80	1333.3	1009.8	200	1652.6	1067.1

[a] Density above 110 or 108.3 MPa was estimated from Eq. (5).

Table II. *(Continued)*

p (MPa)	u ($m \cdot s^{-1}$)	ρ ($kg \cdot m^{-3}$)	p (MPa)	u ($m \cdot s^{-1}$)	ρ ($kg \cdot m^{-3}$)
PDMS-50					
298.15 K					
0.1	1003.2	960.0	88.6	1380.1	1029.8
5.1	1035.8	966.0	98.4	1410.5	1035.2
10.0	1061.2	970.8	108.3	1440.8	1041.0
14.9	1089.9	976.1	118.2	1467.3	1045.9
19.8	1113.3	980.1	128.0	1493.6	1050.8
24.7	1138.2	984.9	137.8	1519.4	1055.6
29.6	1160.2	989.2	147.7	1545.0	1060.4
39.4	1202.9	997.0	157.6	1569.3	1064.9
49.3	1243.3	1004.8	167.5	1593.5	1069.4
59.1	1279.2	1011.8	177.3	1616.6	1073.7
68.9	1316.1	1018.4	187.2	1640.1	1078.0
78.7	1349.4	1024.3	197.2	1661.6	1082.0
303.15 K					
0.1	989.8	955.0	88.6	1371.7	1026.0
5.1	1022.2	960.1	98.4	1401.3	1031.0
10.0	1047.7	964.7	108.3	1431.0	1037.2
14.9	1073.7	970.7	118.2	1458.6	1042.4
19.8	1103.0	974.9	128.0	1487.1	1047.8
24.7	1124.6	979.6	137.9	1511.1	1052.3
29.6	1147.8	984.1	147.7	1537.4	1057.2
39.4	1192.0	992.6	157.6	1562.1	1061.9
49.3	1232.9	1000.7	167.5	1586.1	1066.4
59.1	1269.5	1007.7	177.4	1608.7	1070.6
68.9	1305.6	1014.0	187.3	1631.8	1075.0
78.7	1340.4	1020.0	197.2	1653.6	1079.1
308.15 K					
0.1	976.7	950.1	88.6	1362.9	1022.1
5.1	1008.3	955.0	98.4	1393.4	1027.4
10.0	1036.8	960.0	108.3	1422.8	1033.5
14.9	1063.0	965.8	118.2	1449.9	1038.6
19.8	1091.5	970.6	128.0	1478.7	1044.0
24.7	1114.3	975.4	137.9	1505.4	1049.0
29.6	1138.9	979.9	147.7	1530.0	1053.7
39.5	1182.6	988.5	157.6	1556.0	1058.6
49.3	1222.2	996.3	167.5	1579.9	1063.1
59.1	1261.3	1000.3	177.4	1601.9	1067.2
68.9	1296.5	1010.2	187.3	1625.1	1071.6
78.8	1331.0	1016.0	197.2	1645.6	1075.5

The experimental values for the ultrasonic speeds u and the densities ρ for PDMS-30 and PDMS-50 at temperatures of 298.15, 303.15, and 308.15 K are listed in Table II. Weissler [13] observed the physical properties for PDMS (Dow Corning Silicon Oil DC-500) at atmospheric pressure and reported 981.6 $\mathrm{m \cdot s^{-1}}$ and 954.0 $\mathrm{kg \cdot m^{-3}}$ at 303.15 K as the values of u and ρ for PDMS-50, respectively. These values are slightly lower than those in the present results. Figure 3 illustrates graphically the relative speed u/u_0 for PMDS as a function of pressure. These values for both samples seem to increase smoothly with increasing pressure, showing almost the same tendency. However, when the figure is enlarged these u curves cross at a low pressure. For each temperature, the experimental results are

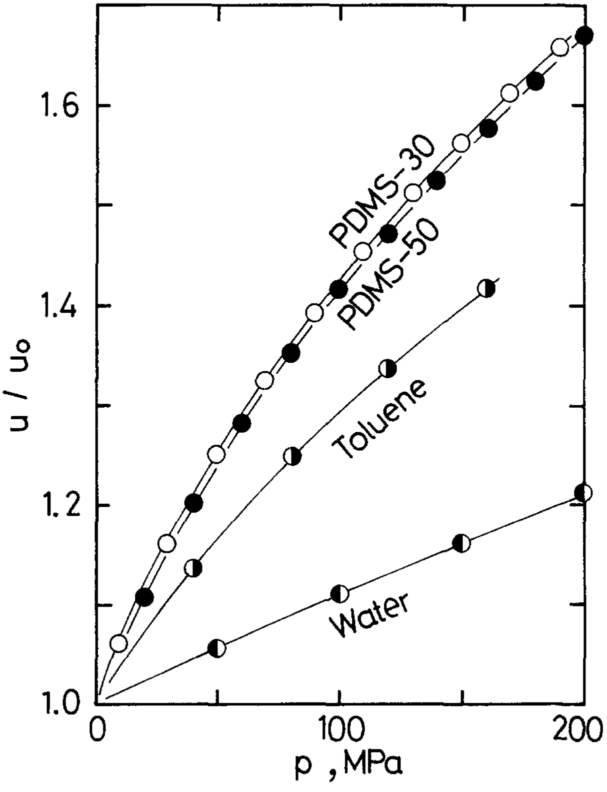

Fig. 3. Pressure dependence of relative ultrasonic speed u/u_0 in PDMS, toluene [7], and water [14] at 303.15 K.

used to determine the values of coefficients in the following equation by means of the least-squares method:

$$u = u_0 + \sum_{i=1}^{4} a_i[p/(MPa)]^i \tag{4}$$

where u is in $\mathrm{m \cdot s^{-1}}$. The coefficients a_i and maximum deviations are given in Table III.

In Fig. 4 the relative densities ρ/ρ_0 for PDMS are plotted against pressure. The densities increase with increasing pressure, similar to the behavior of the u value described above. From Figs. 3 and 4, it becomes apparent that the difference between the absolute values of u and ρ for PDMS-30 and those for PDMS-50 is very small. The pressure dependences of u and ρ for both fluids are nearly equal. However, the u and ρ values for

Table III. Coefficients a and b in Eqs. (1) and (2) and Maximum Deviations $\delta_{\max}$ from the Equations

	298.15 K	303.15 K	308.15 K
		PDMS-30	
u_0	1002.03	988.33	974.88
a_1	5.98962	6.13018	6.23032
$10^{-2}a_2$	−2.75741	−2.92315	−3.01656
$10^{-4}a_3$	1.07771	1.17017	1.20864
$10^{-7}a_4$	−1.83079	−2.01389	−2.06084
$\delta_{\max}$ (%)	0.24	0.18	0.29
b_0	997.49	989.44	978.28
b_1	5.419	5.420	5.403
$\sigma_{\max}$ (%)	0.57	0.26	0.23
		PDMS-50	
u_0	1004.54	990.31	976.69
a_1	6.00296	6.08461	6.29338
$10^{-2}a_2$	−2.83294	−2.86517	−3.23515
$10^{-4}a_3$	1.12636	1.13347	1.41435
$10^{-7}a_4$	−1.91079	−1.93219	−2.64112
$\delta_{\max}$ (%)	0.19	0.23	0.13
b_0	1004.01	993.04	980.69
b_1	5.389	5.324	5.303
$\delta_{\max}$ (%)	0.16	0.32	0.41

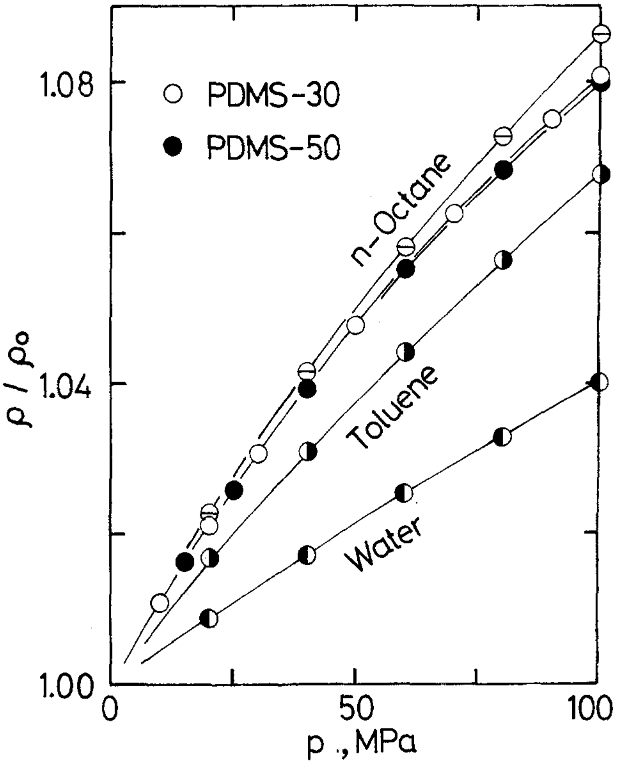

Fig. 4. Pressure dependence of relative density ρ/ρ_0 for PDMS, toluene [7], *n*-octane [10], and water [15] at 303.15 K.

PDMS are affected by pressure more strongly than the u and ρ values for water [14, 15] and toluene [16].

For organic liquids, the relation between u and ρ at a constant temperature satisfies a first-order relation as reported in our previous papers [3, 6]. The same relation is observed for PDMS, as shown in Fig. 5. This relation is expressed by the following equation:

$$u = b_0 + b_1(\rho - \rho_0) \tag{5}$$

where u is in $\text{m} \cdot \text{s}^{-1}$ and ρ_0 is the density at atmospheric pressure. The coefficient b_1 is obtained by means of the least-squares method and is also listed in Table III with the value of the maximum deviations from the equation.

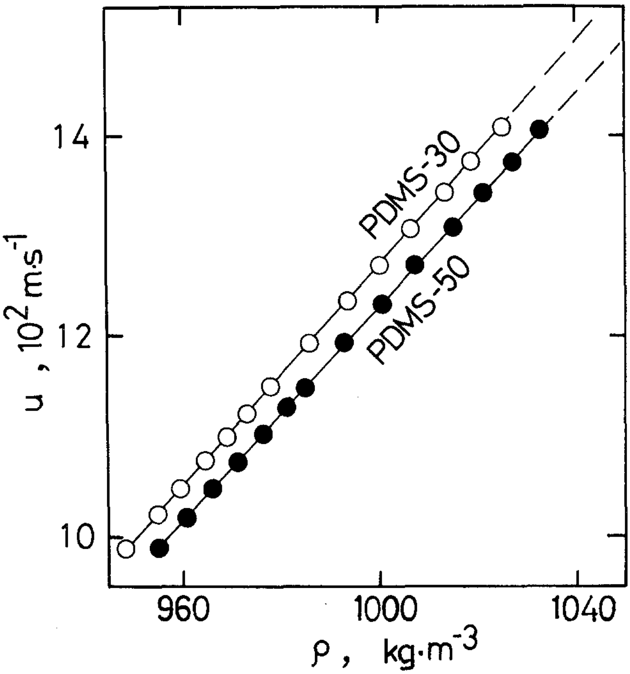

Fig. 5. Ultrasonic speed u against density ρ for PDMS at 303.15 K.

From the results of new measurements on ultrasonic speed u and density ρ, we calculated the isentropic compressibility κ_S by

$$\kappa_S = 1/(\rho \cdot u^2) \tag{6}$$

where the densities at each pressure above 100 MPa were estimated by Eq. (5) using the speed under the same condition. The results at 303.15 K are shown in Fig. 6 as a function of pressure. The effect of pressure on κ_S for PDMS is nearly equal to that for *n*-octane [16]. The effect of pressure on κ_S for PDMS is much larger than that for toluene or water and is similar to the pressure effects on the speed and density.

According to Eyring's free volume theory [17], when the value for the free volume in liquid is large, i.e., the intermolecular free length is long, the ultrasonic speed shows a small value [18]. From this model, it may be presumed qualitatively that the intermolecular free length of PDMS, which is polymer fluid, will be much larger at atmospheric pressure than that of a molecule with a nearly spherical shape such as a hydrocarbon. From this model we expect the ultrasonic speed to be small and the compressibility to be large. The large pressure effects described above result from decreases in this free length or volume.

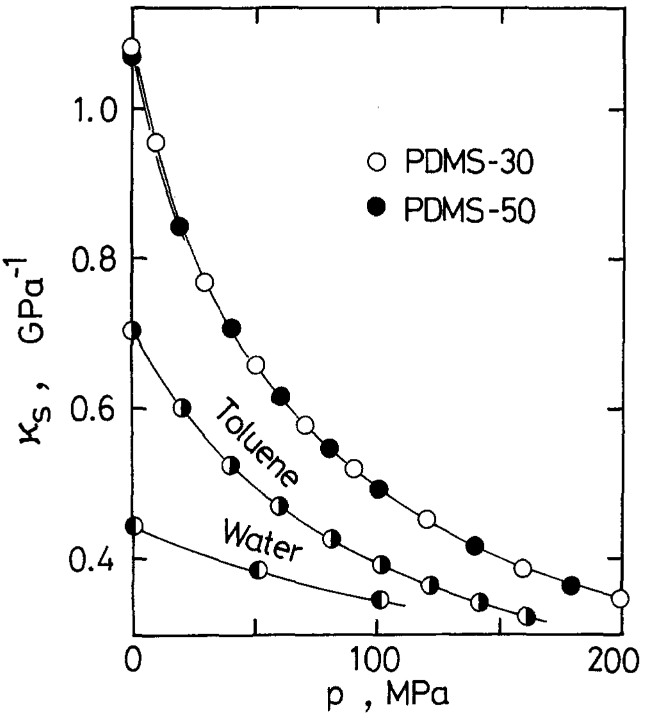

Fig. 6. Pressure dependence of isentropic compressibility κ_S for PDMS, toluene, and water at 303.15 K. κ_S for toluene and water derived from values of u [7, 14] and ρ [7, 15].

4. CONCLUSIONS

A new apparatus using the sing-around technique and employing a fixed-path interferometer with a single transducer is convenient and accurate for the measurement of ultrasonic speed. A new piezometer using an ultrasonic transducer for measuring the displacement of a bellows is convenient and accurate for the measurement of density. The ultrasonic speed and density for poly(dimethylsiloxane) were measured at temperatures of 298.15, 303.15, and 308.15 K and pressures up to 200 or 100 MPa. The results at a constant temperature have a smooth change with pressure and show a large pressure dependence. The linear relation between the ultrasonic speed and the density accompanying a rise in pressure is found to hold well. From this relation, either the ultrasonic speed or the density under higher pressures can be derived accurately using Eq. (5) when the other value is known. The isentropic compressibility for PDMS, calculated from the experimental values, has a strong pressure dependence, especially in the lower-pressure region. The pressure behavior of the present quantities is discussed qualitatively with Eyring's free-volume model.

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