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ULTRASONIC SPEEDS AND THERMODYNAMIC PROPERTIES FOR TETRAMETHYLSILANE, TETRAETHYLSILANE AND TETRAETHOXYSILANE UNDER HIGH PRESSURES

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ABSTRACT

Ultrasonic speeds u in tetramethylsilane TMS, tetraethylsilane TES and tetraethoxysilane TOS were measured by a "sing-around" technique operated at a frequency of 2 MHz. The present results cover temperatures from 283.15 to 333.15 K and pressures up to 200 MPa for TMS and 100 MPa for the other two liquids, with an observed error of less than ±0.3%. The u values for these compounds, affected more largely by temperature and pressure changes than those for toluene and poly(dimethylsiloxane), show that the order of magnitude is TMS < TOS < TES, which differs from that for the densities reported elsewhere. Among the compounds studied, the pressure effects on the u values in TMS and TES are notably larger than those in TOS, in spite of the fact that the densities of TOS displayed a larger pressure effect than did the densities of TES. It was found that the order of magnitude of numerical u value and the pressure effect on the ultrasonic speeds correspond excellently to those on the intermolecular free lengths derived by Eyring's liquid model using pVT.

INTRODUCTION

The temperature and pressure effects on ultrasonic speed, pVT and related thermodynamic properties of some organic liquids have been extensively studied in our laboratories [1–5]. In this research, it was found that for the silicon compound poly(dimethylsiloxane) PDMS the unique behaviour of each quantity was indicated by temperature and pressure changes [5]. Parkhurst and Jonas [6] measured the pVT and the NMR spectra for tetramethylsilane and benzene under high pressure, and discussed the pressure effects on the self-diffusion coefficients of these compounds. Munoz et al. [7] also measured the electron mobility for n-hexane, 2,2-dimethylbutane and tetramethylsilane under pressures up to 300 MPa. They also proved that for tetramethylsilane, which is a silicon compound, the variations of these

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quantities with pressure differ clearly from those of other hydrocarbon liquids. However, systematic studies on the thermodynamic properties at high pressures of organic liquids containing silicon atoms have seldom been reported.

In an earlier paper [8], the authors reported the *pVT* for three silicon compounds: tetramethylsilane TMS, tetraethylsilane TES and tetraethoxylsilane TOS, which are spherical or symmetrical molecules, under pressures up to 100 MPa. As part of a series of studies on the thermodynamic properties of silicon compounds, this paper reports the experimental measurements of ultrasonic speeds in the same compounds. The temperature and pressure effects of ultrasonic speeds and related properties which depend on the differences in molecular structure in these three silicon compounds are discussed, together with the effects on those for toluene and PDMS [4].

EXPERIMENTAL

Aldrich NMR Grade tetramethylsilane $Si(CH_3)_4$, purity 99 + mol %, and Shinetsu Research Grade tetraethylsilane $Si(C_2H_5)_4$ and tetraethoxysilane $Si(CO_2H_5)_4$ of purities better than 99.8 mol % were used without further purification. The physical properties of these liquids are listed in Table 1.

TABLE 1

Physical properties and intermolecular free length L_f for TMS, TES and TOS at 298.15 K and 0.1 MPa

	TMS	TES	TOS
Chemical formula	$Si(CH_3)_4$	$Si(C_2H_5)_4$	$Si(CO_2H_5)_4$
Density (kg m^{-3})	632.59	763.06	928.24
Freezing temp. T_f(K)	170.9 [a]	190.1 [a]	190.92 [b]
Boiling temp. T_b(K) [c]	299.8	427.9	441.1
Critical temp. T_c(K)	448.64 [a]	603.7 [a]	575.9 [d]
Critical pres. p_c(MPa)	2.821	2.602	–
Liquid volume at T_f [e]	114.96	187.26	199.78
Solid volume at T_f [f]	102.32	158.64	177.81
Solid volume at 0 K [g]	98.22	150.74	176.01
L_f (pm)	94.9	66.4	75.2
$C_p - C_v$($JK^{-1}mole^{-1}$)	45.2	53.5	70.7

[a] ref. 11.

[b] measured in this work.

[c] ref. 19.

[d] estimated from method in ref. 18.

[e] extrapolated values (cm^3 mol^{-1}).

[f] calculated values (cm^3mol^{-1}) from eqn. (5).

[g] calculated values (cm^3mol^{-1}) from eqn. (3).

The method used to measure ultrasonic speed was a "sing-around" technique employing a fixed-path acoustic interferometer of length 31.2341 mm, operated at a frequency of 2 MHz, similar to that described previously [9]. In this study, the temperature in the sample and a thermostat was observed using a T-type thermocouple calibrated with a standard platinum resistance thermometer, and the pressure was observed by a strain gauge up to 200 MPa calibrated with a dead-weight tester. The maximum estimated errors of temperature and pressure were ± 0.03 K and ± 0.08 MPa up to 70 MPa, and ± 0.13 MPa in the range from 70 to 200 MPa respectively. The probable uncertainty in the measurements of the ultrasonic speed is estimated to be no greater than ± 0.6 m s^{-1} at lower pressures and ± 1.8 m s^{-1} at higher pressures.

RESULTS AND DISCUSSION

The experimental ultrasonic speeds u at various temperatures T and pressures p in tetramethylsilane TMS, tetraethylsilane TES and tetraethoxysilane TOS are presented in Table 2. Figure 1(a) shows the results plotted against temperature at atmospheric pressure. Only one previous set of measurements of u in silicon compounds at atmospheric pressure has been reported, that by Kannebley and Schaaffs [10]. The values of u reported in their paper are 1213 and 1076 m s^{-1} in TES and TOS at 293.15 K respectively. Among these, that in TOS is in good agreement with the present result of 1074.5 m s^{-1}, but that in TES is lower by about 10 m s^{-1} than our result of 1222.9 m s^{-1}. In these silicon liquids, the speeds decrease showing an approximately linear relation with the rise in temperature; the curves, for each liquid, however, show slight differences in their temperature dependences. For TMS, the boiling temperature T_b is 300.15 K [11]. Therefore, in the higher temperature region, the speed u_{p_v} at saturated vapour pressure p_v, shown by the dotted line in Fig. 1(a), was estimated by an extrapolation of data at high pressure to that at p_v. The value of the vapour pressure p_v, required for this calculation, was obtained from an equation reported in ref. 12.

The pressure variations of speeds u at 298.15 K are presented in Fig. 1(b) together with those in toluene [3,13] and in poly(dimethylsiloxane), viscosity grade 30×10^{-4} m s^{-1}, PDMS-30 [5], in which there are high pressure dependencies of u. As can be seen in the figure, the speeds u in the compounds studied increase smoothly with increasing pressure, and they depend more strongly on the pressure changes than those for toluene and PDMS. Moreover, the pressure effects of speeds $(\partial u/\partial p)_T$ in these silicon liquids are different from each other. That is, those for TMS and TES show much larger pressure effects than those for TOS, which are in the order of TMS > TES > TOS with respect to $(\partial u/\partial p)_T$. However the magnitude of u

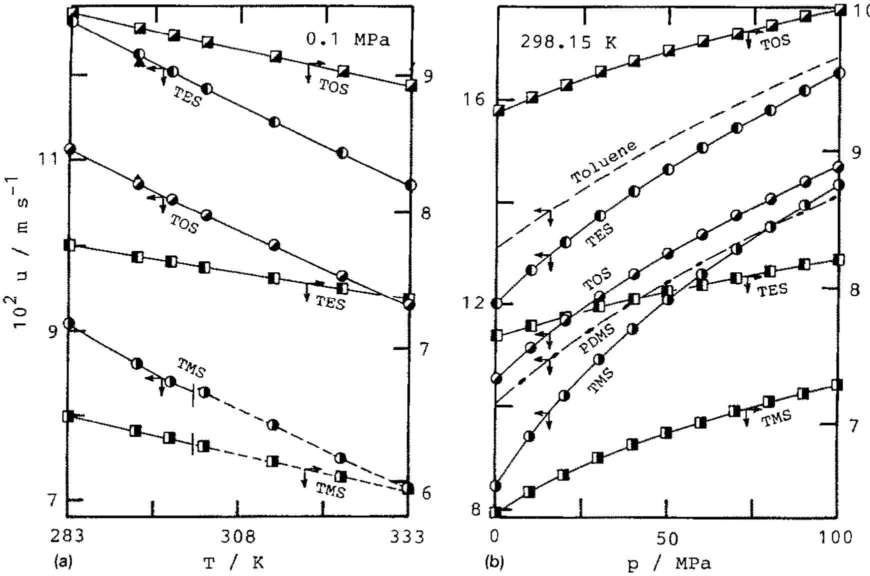

Fig. 1. (a) Temperature dependencies of ultrasonic speeds u and (b) pressure dependence of densities ρ [8], for silicon compounds at 298.15 K: ○, u; □, ρ; — — —, u in toluene [3]; ·—·—·, u in PDMS [5].

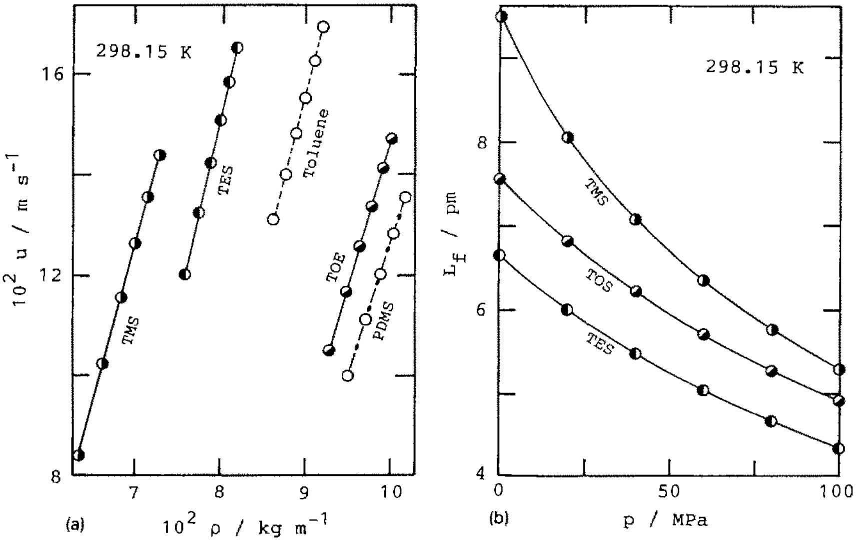

Fig. 2. Relation (a) between ultrasonic speeds u and densities ρ and (b) between intermolecular free lengths L_f and pressure p, for sillicon compounds at 298.15 K: — — —, toluene; ·—·—·, PDMS-30.

TABLE 2

Ultrasonic speeds u in TMS, TES and TOS at various temperatures T and pressures p

p	u(m s^{-1}) at T(K)						
(MPa)	283.15	293.15	298.15	303.15	313.15	323.15	333.15
TMS							
0.1	908.8	862.3	840.4	837.5 [a]	796.2 [a]	755.9 [a]	716.6 [a]
10	1000.0	959.9	940.4	922.7	884.8	847.6	812.3
20	1076.5	1039.7	1022.5	1006.5	972.8	939.7	908.6
30	1143.2	1108.7	1093.2	1078.1	1046.7	1016.3	988.0
40	1202.4	1169.8	1155.3	1141.2	1111.6	1083.1	1057.0
50	1256.5	1225.6	1211.8	1197.8	1170.1	1142.9	1118.4
60	1306.0	1276.4	1263.1	1249.7	1223.0	1197.3	1173.8
70	1352.5	1323.8	1310.9	1297.9	1272.2	1247.5	1224.9
80	1395.5	1368.0	1355.0	1343.1	1317.9	1294.1	1272.0
90	1436.2	1409.4	1397.5	1385.1	1360.9	1337.8	1316.0
100	1474.7	1448.5	1437.0	1425.5	1401.5	1378.9	1357.4
110	1510.9	1485.8	1474.7	1463.5	1440.3	1417.7	1396.7
120	1545.7	1521.2	1510.8	1499.4	1476.8	1454.9	1433.9
130	1579.4	1555.3	1544.8	1533.6	1511.8	1490.1	1470.1
140	1611.4	1587.8	1575.4	1566.7	1545.3	1524.0	1504.4
150	1642.5	1619.3	1607.1	1598.5	1577.2	1556.4	1537.3
160	1672.3	1649.4	1637.5	1629.1	1608.1	1584.6	1568.8
170	1701.2	1678.4	1667.3	1658.7	1637.9	1617.2	1599.2
180	1729.0	1706.5	1695.8	1686.9	1666.8	1647.0	1628.6
190	1755.4	1733.4	1723.9	1714.5	1694.4	1674.9	1657.5
200	1772.3	1761.4	1752.6	1744.5	1724.3	1704.1	1688.6
TES							
0.1	1262.1	1222.9	1203.9	1184.7	1146.5	1097.5	1071.9
10	1320.9	1284.0	1266.3	1248.7	1213.0	1179.1	1145.0
20	1373.9	1339.5	1322.6	1306.1	1272.9	1240.6	1208.9
30	1422.8	1389.9	1374.0	1358.3	1326.6	1296.0	1266.3
40	1468.1	1436.7	1421.4	1406.3	1376.2	1347.0	1319.0
50	1510.6	1480.7	1465.6	1451.1	1422.4	1394.4	1367.1
60	1550.5	1521.5	1506.9	1493.1	1456.1	1438.0	1412.2
70	1588.3	1560.3	1546.6	1532.3	1505.7	1479.4	1454.7
80	1624.7	1598.4	1583.9	1569.5	1544.2	1518.9	1494.7
90	1659.2	1632.2	1619.6	1605.4	1581.0	1556.2	1523.6
100	1692.2	1666.0	1653.3	1639.6	1616.0	1592.0	1568.8
TOS							
0.1	1112.2	1074.5	1056.6	1038.1	1002.0	966.4	931.3
10	1166.8	1132.0	1115.1	1097.9	1064.7	1032.3	1000.2
20	1216.6	1183.2	1167.5	1151.4	1120.0	1089.6	1060.0
30	1261.8	1230.3	1215.1	1199.8	1170.1	1141.5	1113.0
40	1303.8	1273.5	1259.1	1244.6	1216.4	1189.0	1161.7
50	1343.4	1314.1	1300.0	1286.4	1258.8	1232.6	1206.7
60	1380.0	1351.9	1338.4	1325.3	1298.5	1273.1	1248.2
70	1415.2	1387.9	1374.7	1361.8	1336.0	1311.1	1286.6
80	1448.6	1421.9	1409.1	1398.1	1371.6	1347.4	1323.7
90	1480.3	1454.2	1441.7	1430.0	1405.2	1381.8	1358.7
100	1510.9	1485.1	1473.0	1461.9	1436.9	1414.7	1391.9

[a] Estimated values at vapour pressure.

values increases in the order TMS < TOS < TES over the range of experimental conditions.

In organic liquids and their binary mixtures, it is well known that the ultrasonic speeds u are closely related, in most cases, to the densities ρ, and therefore the u values at high pressure are frequently used to obtain pVT for the system [13,14].

For the compounds studied here, the densities had been previously measured by the authors using a glass piezometer [8]; the densities are also plotted in Fig. 1. The magnitude of the observed densities are in the order TMS < TES < TOS over the whole range of conditions, that is, the densities increased corresponding to an increased complexity of molecular structure, as can be seen in this figure. This order, however, is not in agreement with that observed for the magnitude of u values, as described above. Moreover, when the pressure effects of u and ρ for TES are compared with those for TOS, $(\partial u/\partial p)_T$ for TES is larger, but interestingly $(\partial \rho/\partial p)_T$ is smaller than those for TOS.

Figure 2(a) shows the relations between speed and density for these compounds. The speeds in the present compounds clearly indicate a first-order relation with the densities, similar to those reported for some organic compounds [13,15]. However, in this figure, the curve for TOS is widely separated from those of the two other liquids and is located near that of PDMS. In many cases of hydrocarbon liquids, the u against ρ curve falls near that for toluene as indicated in Fig. 2(a). From these facts, the compounds studied here seem to have unusual properties which have been observed in other hydrocarbon liquids.

In order to account for the unusual behaviour of u by differences in the silicon compounds, the intermolecular free length L_f was determined. According to Eyring's liquid free volume theory [16], the acoustic wave, which was generated in the sample liquid for measurement of the ultrasonic speed, is transferred momentarily to the intramolecular length. That in the space of two neighbouring molecules, namely in the intermolecular free length L_f, having different characteristics for different organic compounds, is transferred in accordance with the speed in the gas phase of the liquid. In general, when the value for the free volume in liquid is large i.e. the intermolecular free length is long, the speed has a low value. Now, assuming that the sample liquid has a spherical molecule, the values of L_f can be estimated using the following equation [17]

$$L_f = 2(V_T - V_0)/Y \tag{1}$$

where V_T is the molar volume at temperature T and the molar surface area in molecules, Y, is given by

$$Y = \left(36\pi N V_0^2\right)^{1/3}, \tag{2}$$

where N is Avogadro's number and V_0 is the molar volume at absolute zero temperature. The V_0 value was estimated using the critical temperature T_c by Sugden's empirical equation [18]

$$V_0 = V_T[1-(T/T_c)]^{-1/3}. \tag{3}$$

The values of T_c are 448.68 K for TMS and 603.7 K for TES [11]. But T_c for TOS is not known and so was estimated by Lydersen's method employing a group contribution in the molecular structure [18], giving a T_c value of 575.9 K for TOS. Where the boiling temperature was required in this estimation, the value reported in ref. 19 was used. The molar volume at absolute zero V_0 remains largely unaltered from that at freezing temperature T_f. Thus, in order to check the estimated T_c for TOS, the liquid volume $V_{f(l)}$ at T_f was estimated graphically by the extrapolation of volumes measured previously. For some organic liquids, the volume $V_{f(s)}$ in the solid phase at T_f can be estimated [20] using the equation

$$V_{f(s)} = 0.89\ V_{f(l)} \tag{4}$$

The solidified volumes at T_f and T_0 for TOS, 177.81 and 176.01 cm^3 mol^{-1}, respectively, obtained from eqns. (4) and (3), seem to be reasonable as compared with those for the two other comopunds. The intermolecular free lengths L_f thus obtained at 298.13 K are presented in Fig. 2(b) as a function of pressure. As can be seen in this figure, the L_f value for these liquids decreases with a rise in pressure, i.e. the decrease of L_f contributes to the increase of u. Also, on each isobar in Fig. 2(b), the order of the L_f curves is TES < TOS < TMS, which order corresponds well to the reverse order of u seen in Fig. 1. From the comparison of the apparent L_f described above, the behaviour of the speeds resulting from the temperature and pressure change in these silicon compounds can be explained quantitatively on the basis of Eyring's liquid free volume theory.

From the ultrasonic speed u and the pVT relation, the isentropic compressibility, $\kappa_S = [(\rho u^2)^{-1}]$, and the ratio of heat capacities, $\gamma = [-(u^2/V^2)(\partial V/\partial p)_T]$, where V is the specific volume, were derived. Figure 3 shows the pressure effects on κ_S and γ at 298.15 K. For some organic compounds, the κ_S values usually appeared to be about 0.6 GPa^{-1} at atmospheric pressure, except those for n-alkanes. However, the κ_S values for the silicon compounds presented here are extremely large, especially that for TMS, and these values depend strongly on the pressure change as is the case with the speed. This behaviour may be affected by a large intermolecular free volume V_f, i.e. a large L_f.

Of the three silicon compounds, the density and its pressure effect are larger for tetraethoxysilane, but the speed and its pressure dependence are smaller than in the other compounds.

The difference between the molar heat capacities at constant pressure and constant volume, $C_p - C_v$, which is one of the measures of intermolecular interaction, was calculated thermodynamically from pVT. As listed in Table

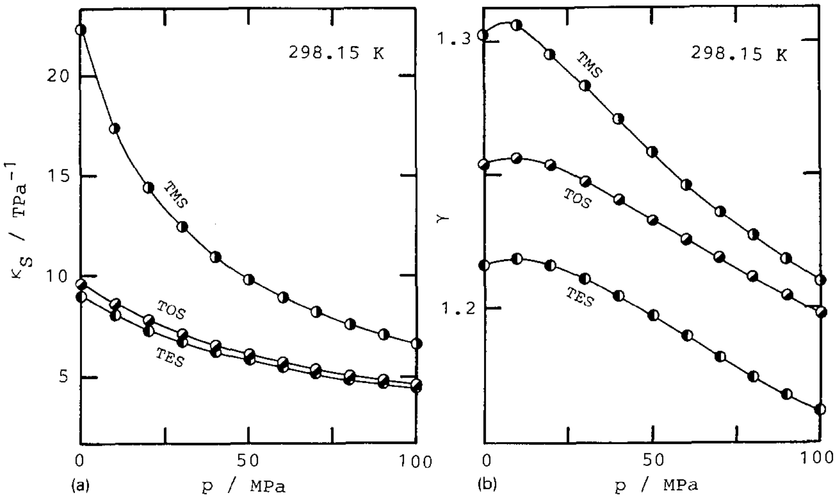

Fig. 3. Pressure dependence of (a) isentropic compressibilities κ_S and (b) ratio of heat capacities γ, for silicon compounds at 298.15 K.

1, $C_p - C_v$ for TOS is larger than those for the other two liquids, which suggests a relatively larger intramolecular interaction. For tetraethoxysilane, the -Si-C-O-O- bonding is stable. That is, the bond energy appears to be higher than those of -Si-C- or -Si-C-C- bonds for TMS and TES. Consequently, the thermodynamic properties of TOS differ from those of the other silicon compounds studied, TMS and TES.

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