International Journal of Thermophysics, Vol. 11, No. 3, 1990

Densities of Tetramethylsilane, Tetraethylsilane, and Tetraethoxysilane Under High Pressures

C. Yokoyama,[1] T. Takagi,[2] and S. Takahashi[1]

Received June 22, 1989

Accurate density data for tetramethylsilane, tetraethylsilane, and tetraethoxysilane in the temperature range from 283.15 to 333.15 K under pressure up to 100 MPa have been measured in order to test existing correlation methods. We have also measured the saturated liquid densities of tetramethylsilane, tetraethylsilane, and tetraethoxysilane in the temperature range from 283 to 343 K. The modified Rackett equation and the COSTAD correlation were used to correlate the saturated liquid density data. The Tait equation and a modified van der Waals equation of state were used to correlate the liquid density data under pressure. It was found that the average absolute deviations of the experimental values from those calculated with the Tait equation and the modified van der Waals equation of state were less than 0.01 and 0.21%, respectively. The effective hard sphere diameters for these three silane compounds were determined from the modified van der Waals equation of state parameter. It was found that the effective hard-sphere diameter decreases with temperature.

KEY WORDS: density; equation of state; high pressure; Tait equation; tetraethylsilane; tetraethoxysilane; tetramethylsilane.

1. INTRODUCTION

PVT relationships are important for the correlation of transport properties, ultrasonic speed of sound, and related thermophysical properties.

Takagi and Teranishi [1] measured the ultrasonic speed and *pvt* relationships of poly(dimethylsiloxane) under high pressures and found

---

[1] Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai 980, Japan.

[2] Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Kyoto 606, Japan.

0195-928X/90/0500-0477$06.00/0 © 1990 Plenum Publishing Corporation

that each quantity indicated unique behavior with temperature and pressure changes. It was also found that the pressure dependences of the self-diffusion coefficient and the electron mobility for tetramethylsilane under high pressures differ clearly from those for other hydrocarbon liquids [2, 3]. However, thermophysical properties for silicon compounds have not been measured extensively.

As a part of serial studies on thermophysical properties of silicon compounds, this paper reports experimental results of the *pvt* relationships for three silicon compounds: tetramethylsilane (TMS), tetraethylsilane (TES), and tetraethoxysilane (TOS). The ultrasonic speeds of these silicon compounds under pressure were investigated and the temperature and pressure effects of ultrasonic speeds and related quantities depending on the molecular structure were discussed by Takagi et al. [4]. Since these silicon compounds can be assumed to be spherically symmetric, the *pvt* relationships of these compounds are needed to investigate the validity of theoretical equations for the thermophysical properties for simple molecular fluids.

Parkhurst and Jonas [2] measured the densities of TMS over a temperature range from 298.15 to 373.15 K at pressures from 4 to 450 MPa and reported the constants of the Tait equation. The saturated liquid densities for TMS were measured by McGlashan and McKinnon [5] over the temperature range from 373.07 to 448.62 K. Saturated liquid densities and liquid densities under high pressures for TES and TOS have not been measured.

2. EXPERIMENTAL

The liquid densities of TMS, TES, and TOS under pressures were measured using a glass piezometer. The details of the apparatus and experimental procedures were described previously [6, 7].

The saturated liquid density was determined by measuring the volume of the sample in a sealed dilatometric tube. The dilatometric tube was made of borosilicate glass and consisted of a capillary (4-mm i.d. and 100-mm length) and a bulb (about 16-cm^3 volume). The volume of the tube was calibrated using mercury to an uncertainty of less than 0.01 %. A syringe with a 150-mm needle was used to deliver the sample into the bulb. After the sample was loaded, the tube was connected to the vacuum line through a silicon rubber tube, and the sample was degassed. During degassing, the sample in the bulb was cooled with cold methanol. After degassing, the capillary was fused about 100 mm from the bulb, while the tube was still connected to the vacuum line. The sample mass was determined by weighing the tube before and after loading the sample. The tube was held vertically in a thermostat equipped with a window to allow viewing of the capillary.

The volume of the sample was determined from the measurement of the liquid level of the sample in the capillary. The liquid level was measured with a cathetometer with an uncertainty of ±0.002 mm. The mass of sample in the liquid was corrected for vaporization loss. The mass of sample vaporized was determined by the volume of the gas phase, the vapor pressure of the sample, the molar mass of the sample, and the ideal gas law. The ratio of the mass of the vaporized sample and that of the loaded sample was less than 0.01% for the present experimental condition. The vapor pressures were those given by Aston et al. [8] for TMS and by Perry and Chilton [9] for TES and TOS. The probable uncertainty in the measurements of the saturated liquid density is estimated to be no greater than $0.0002\ \mathrm{g \cdot cm^{-3}}$.

The temperature of the thermostat was observed with a mercury thermometer calibrated with a Leeds–Northrup platinum resistance thermometer. The pressure of the sample was observed using a Heise bourdon-tube gauge, which was calibrated with a deadweight tester. The details of the deadweight tester were described by Toriumi et al. [10]. The uncertainty of the pressure measurement with the deadweight tester was within 0.02%. The maximum estimated errors of temperature and pressure measurements were ±0.01 K and ±0.05 MPa up to 70 MPa and ±0.1 MPa in the range from 70 to 100 MPa, respectively. The probable uncertainty in the measurements of the liquid density under high pressures was estimated to be no greater than $0.0002\ \mathrm{g \cdot cm^{-3}}$.

Aldrich NMR-grade tetramethylsilane, purity 99+ mol%, and Shinetsu research-grade tetraethylsilane and tetraethoxysilane, purities better than 99.8 mol%, were used without further purification.

3. RESULTS

The saturated liquid density data of TMS, TES, and TOS are listed in Table I. These data are correlated by the following polynomial equation.

$$\rho = a_1 + a_2 T + a_3 T^2 \tag{1}$$

The values of the coefficients, a_i, and the deviations of the calculated values from the experimental data are shown in Table II. The densities under pressure are shown in Table III. The absolute average deviations of the experimental values of TMS from the calculated values with the Tait equation of Parkhurst and Jonas [2] are 0.56% at 298.15 K and 0.27% at 323.15 K.

Table I. Saturated Liquid Densities for TMS, TES, and TOS

TMS		TES		TOS	
T (K)	ρ ($g \cdot cm^{-3}$)	T (K)	ρ ($g \cdot cm^{-3}$)	T (K)	ρ ($g \cdot cm^{-3}$)
280.74	0.6523	278.13	0.7773	283.13	0.9439
287.26	0.6443	283.39	0.7746	285.13	0.9418
287.97	0.6435	287.25	0.7717	287.37	0.9399
292.48	0.6386	291.14	0.7689	291.28	0.9355
297.63	0.6329	294.25	0.7665	293.24	0.9335
302.78	0.6274	297.76	0.7633	296.21	0.9302
304.65	0.6254	299.94	0.7615	298.15	0.9286
312.35	0.6165	303.24	0.7591	300.71	0.9256
314.19	0.6143	306.08	0.7567	303.15	0.9231
317.70	0.6101	309.68	0.7540	308.15	0.9177
322.25	0.6046	311.93	0.7521	313.15	0.9127
327.62	0.5981	315.84	0.7492	318.15	0.9075
342.18	0.5811	319.60	0.7463	323.15	0.9021
		324.84	0.7428	325.31	0.9002
		326.12	0.7421	328.15	0.8973
		328.22	0.7406	333.31	0.8919
		332.40	0.7376		
		333.89	0.7365		
		336.55	0.7344		

4. CORRELATION

The saturated liquid density was correlated with the modified Rackett equation proposed by Spencer and Danner [11] and the COSTAD equation proposed by Hankinson and Thomson [12].

The modified Rackett is expressed as follows:

$$\rho = [P_c/RT_c] Z_{RA}^{-[1-(1-T_r)^{2/7}]} \tag{2}$$

Table II. Coefficients of Eq. (1) for the Saturated Liquid Densities for TMS, TES, and TOS

Compound	Temp. range (K)	$10\,A_1$ ($g \cdot cm^{-3}$)	$10^4 A_2$ ($g \cdot cm^{-3} \cdot K^{-1}$)	$10^7 A_3$ ($g \cdot cm^{-3} \cdot K^{-2}$)	$10^2 \delta^a$ (%)
TMS	280–343	8.6430	−4.323	−11.577	3.6
TES	278–337	10.6658	−12.683	8.369	3.7
TOS	283–334	11.8769	−7.090	−5.385	2.0

[a] Absolute average deviation of the experimental saturated liquid density values from the values calculated with Eq. (1).

Table III. Densities for TMS, TES, and TOS Under Pressure (P in MPa, ρ in $g \cdot cm^{-3}$, T in K)

	ρ, at T						
P	283.15	293.15	298.15	303.15	313.15	323.15	333.15
				TMS			
0.1	0.6495[a]	0.6380[a]	0.6324[a]	0.6270[b]	0.6154[b]	0.6032[b]	0.5913[b]
10	0.6637	0.6536	0.6489	0.6439	0.6340	0.6234	0.6149
20	0.6760	0.6665	0.6621	0.6581	0.6488	0.6398	0.6325
30	0.6869	0.6777	0.6738	0.6700	0.6615	0.6532	0.6469
40	0.6966	0.6878	0.6840	0.6806	0.6725	0.6648	0.6592
50	0.7049	0.6963	0.6929	0.6897	0.6821	0.6746	0.6697
60	0.7125	0.7045	0.7009	0.6979	0.6906	0.6837	0.6790
70	0.7196	0.7119	0.7085	0.7058	0.6988	0.6920	0.6878
80	0.7262	0.7186	0.7156	0.7129	0.7061	0.6996	0.6957
90	0.7325	0.7249	0.7220	0.7194	0.7128	0.7065	0.7029
100	0.7380	0.7307	0.7279	0.7254	0.7190	0.7131	0.7097
				TES			
0.1	0.7748[a]	0.7674[a]	0.7631[a]	0.7591[a]	0.7513[a]	0.7441[a]	0.7371[a]
10	0.7818	0.7751	0.7710	0.7673	0.7600	0.7533	0.7469
20	0.7885	0.7820	0.7782	0.7745	0.7677	0.7614	0.7554
30	0.7950	0.7887	0.7850	0.7817	0.7752	0.7692	0.7635
40	0.8010	0.7947	0.7912	0.7879	0.7818	0.7763	0.7708
50	0.8062	0.8004	0.7970	0.7938	0.7878	0.7825	0.7773
60	0.8115	0.8057	0.8022	0.7991	0.7932	0.7882	0.7835
70	0.8162	0.8106	0.8072	0.8043	0.7987	0.7939	0.7894
80	0.8207	0.8154	0.8121	0.8093	0.8038	0.7991	0.7950
90	0.8252	0.8200	0.8168	0.8139	0.8085	0.8040	0.8000
100	0.8294	0.8243	0.8211	0.8183	0.8131	0.8085	0.8048
				TOS			
0.1	0.9439[a]	0.9336[a]	0.9287[a]	0.9232[a]	0.9128[a]	0.9022[a]	0.8922[a]
10	0.9534	0.9439	0.9394	0.9342	0.9244	0.9145	0.9051
20	0.9622	0.9531	0.9488	0.9440	0.9347	0.9257	0.9170
30	0.9707	0.9617	0.9576	0.9531	0.9442	0.9359	0.9278
40	0.9782	0.9698	0.9659	0.9615	0.9532	0.9452	0.9376
50	0.9853	0.9772	0.9736	0.9690	0.9612	0.9535	0.9463
60	0.9919	0.9840	0.9804	0.9762	0.9686	0.9612	0.9544
70	0.9981	0.9905	0.9870	0.9830	0.9758	0.9685	0.9619
80	1.0043	0.9969	0.9936	0.9896	0.9822	0.9755	0.9689
90	1.0097	1.0027	0.9995	0.9956	0.9886	0.9819	0.9756
100	1.0158	1.0084	1.0049	1.0012	0.9944	0.9880	0.9820

[a] Interpolated value.
[b] Extrapolated value.

Table IV. Physical Properties for TMS, TES, and TOS

	TMS	TES	TOS
Chemical formula	$Si(CH_3)_4$	$Si(C_2H_5)_4$	$Si(OC_2H_5)_4$
Normal boiling temp. (K)[a]	299.8	427.9	441.1
Critical temp. (K)	448.64[b]	603.7[b]	575.9[c]
Critical pressure (MPa)	2.821[b]	2.602[b]	1.897[c]
Acentric factor[d]	0.241	0.474	0.822

[a] Ref. 17.
[b] Ref. 15.
[c] Ref. 16.
[d] Ref. 14.

where P_c is the critical pressure, R is the gas constant, T_c is the critical temperature, Z_{RA} is a parameter, and T_r is a reduced temperature, T/T_c.

The COSTAD equation is expressed as follows:

$$1/\rho = V^* V_R^{(0)}[1 - \omega_{SRK} V_R^{(1)}] \tag{3}$$

where V^* is a characteristic volume, ω_{SRK} is the acentric factor which forces the Soave equation [13] to give a best fit of vapor pressure data, and $V_R^{(0)}$ and $V_R^{(1)}$ are the functions of T_r given by Hankinson and Thomson [12].

Z_{RA} in the modified Rackett equation and V^* in the COSTAD equation were determined by fitting the experimental data. In calculations with the COSTAD equation, acentric factors calculated with the Lee and Kesler equation [14] were adopted for ω_{SRK}. The physical properties used in this study were listed in Table IV. The values of the critical temperature and pressure for TMS and TES were quoted from Ambrose [15]. However, the critical properties of TOS have not been reported. These values were estimated by Lydersen's method employing a group contribution in molecular structure [16]. The normal boiling temperatures were quoted

Table V. Modified Rackett Equation Correlation for TMS, TES, and TOS

Compound	No. of points	Z_{RC}	Max. dev. (%)	Av. abs. dev. (%)	Bias dev. (%)
TMS	13	0.2728	0.40	0.09	0.01
TES	19	0.2797	0.11	0.06	−0.02
TOS	16	0.2629	0.08	0.03	0.00

Table VI. COSTAD Equation Correlation for Saturated Liquid Densities for TMS, TES, and TOS

Compound	No. of points	V^* ($\mathrm{L \cdot mol^{-1}}$)	Max. dev. (%)	Av. abs. dev. (%)	Bias dev. (%)
TMS	13	4.107	0.31	0.05	−0.03
TES	19	4.077	0.20	0.05	−0.05
TOS	16	3.628	0.12	0.06	−0.06

from Weast and Astle [17]. The values of Z_{RA} and correlation results with the modified Rackett equation are shown in Table V. The values of V^* and correlation results with the COSTAD equation are shown in Table VI. It can be seen that both equations give almost the same correlation results.

The densities under high pressures were correlated with the Tait equation and a modified van der Waals equation of state. The Tait equation can be expressed as follows:

$$(\rho-\rho_0)/\rho = C\ln[(B+P)/(B+P_0)] \tag{4}$$

Table VII. Tait Correlation for TMS, TES, and TOS

Compound	Temp. (K)	B (MPa)	C	Max. dev. (%)	Av. abs. dev. (%)	Bias dev. (%)
TMS	283.15	36.961	0.091938	0.05	0.02	−0.01
	293.15	33.398		0.03	0.01	0.00
	298.15	31.384		0.05	0.02	−0.00
	303.15	29.442		0.03	0.01	−0.01
	313.15	26.208		0.03	0.01	−0.00
	323.15	22.913		0.05	0.02	−0.01
	333.15	19.317		0.05	0.02	0.01
TES	283.15	86.266	0.085549	0.04	0.01	−0.00
	293.15	80.508		0.02	0.01	−0.00
	298.15	77.736		0.02	0.01	−0.00
	303.15	75.012		0.03	0.01	0.00
	313.15	69.695		0.03	0.01	0.01
	323.15	64.562		0.04	0.01	−0.00
	333.15	59.675		0.04	0.01	−0.00
TOS	283.15	81.716	0.088240	0.04	0.01	−0.00
	293.15	75.813		0.02	0.01	−0.00
	298.15	73.141		0.03	0.01	0.01
	303.15	70.145		0.02	0.01	−0.00
	313.15	64.935		0.02	0.01	0.00
	323.15	59.478		0.03	0.01	0.00
	333.15	54.805		0.04	0.01	−0.00

where P and P_0 are a system pressure and a reference pressure, respectively, ρ and ρ_0 are densities at the corresponding pressures, and B and C are parameters. The reference pressure, P_0, was set to be 0.1 MPa. The values of B and C were determined by fitting density values to the experimental data. As pointed out by Dymond and Malhotra [18], it was found that C can be considered constant. A comparison between densities calculated with the Tait equation and the experimental data is given in Table VII. It was found that the Tait equation can fit all the data with an average absolute deviation of 0.05%.

A modified van der Waals equation of state is expressed with the Carnahan-Starling hard-sphere equation of state [19].

$$P = (RT/V)(1 + y + y^2 - y^3)/(1 - y)^3 - a/V^2 \tag{5}$$

where T is the temperature, and V is the molar volume. The reduced density, y, is defined by

$$y = N_A \pi \sigma^3 / 6V \tag{6}$$

Table VIII. Modified van der Waals Equation of State Correlation for TMS, TES, and TOS

Compound	Temp. (K)	a (MPa · L^2 · mol^{-2})	σ (nm)	Max. dev. (%)	Av. abs. dev. (%)	Bias dev. (%)
TMS	283.15	0.3583	5.897	0.58	0.26	0.25
	293.15	0.3534	5.888	0.73	0.35	0.34
	298.15	0.3491	5.880	0.85	0.42	0.42
	303.15	0.3444	5.871	1.00	0.53	0.53
	313.15	0.3387	5.870	0.88	0.42	0.41
	323.15	0.3299	5.843	1.43	0.77	0.77
	333.15	0.3161	5.811	1.88	1.01	1.01
TES	283.15	1.0158	6.990	0.03	0.01	0.00
	293.15	1.0015	6.981	0.09	0.06	0.06
	298.15	0.9939	6.977	0.11	0.07	0.07
	303.15	0.9885	6.976	0.09	0.04	0.03
	313.15	0.9736	6.968	0.14	0.06	0.05
	323.15	0.9567	6.956	0.24	0.11	0.11
	333.15	0.9369	6.943	0.25	0.12	0.11
TOS	283.15	1.2676	7.424	0.11	0.03	−0.02
	293.15	1.2477	7.417	0.06	0.02	−0.02
	298.15	1.2396	7.415	0.04	0.01	−0.01
	303.15	1.2282	7.411	0.04	0.02	0.02
	313.15	1.2073	7.405	0.06	0.04	0.04
	323.15	1.1805	7.394	0.10	0.04	0.04
	333.15	1.1579	7.384	0.16	0.09	0.09

Table IX. Coefficients of Eq. (7) for the Effective Hard-Sphere Diameter for TMS, TES, and TOS

Compound	Temp. range (K)	f (nm)	$10^3 g$ (nm · K^{-1})	$10^2 \delta^a$ (%)
TMS	280–343	6.3625	−1.6198	9.4
TES	278–337	7.2472	−0.9033	2.9
TOS	283–334	7.6499	−0.7915	1.9

[a] Absolute average deviation of the effective hard-sphere diameter values from the values calculated with Eq. (7).

where N_A is Avogadro's constant, and σ is an effective hard sphere diameter. The parameter a in Eq. (5) takes into account the effect of the attractive interaction among the molecules. The values for a and σ were determined with the method proposed by Ewing and Marsh [20] using the *pvt* data at 0.1 MPa and the isothermal compressibility data at 0.1 MPa. The isothermal compressibility at 0.1 MPa was obtained from the Tait equation, Eq. (4). The values for a and σ and a comparison between densities calculated with Eq. (5) and experimental data are given in Table VIII. It was found that the modified van der Waals equation of state can fit the data with an average absolute deviation of 0.2%. The effective hard-sphere diameter can be expressed by the following linear function of temperature:

$$\sigma = f + gT \tag{7}$$

The values of coefficients, f and g, are listed in Table IX. It was found that the effective hard-sphere diameters of the silicon compounds decrease with temperature. This temperature dependence was consistent with those of Bienkowski and Chao [21], del Rio and de Longi [22], and Nezbeda and Aim [23].

REFERENCES

1. T. Takagi and H. Teranishi, *Int. J. Thermophys.* **6**:451 (1985).
2. H. J. Parkhurst, Jr., and J. Jonas, *J. Chem. Phys.* **63**:2698 (1975).
3. R. C. Munoz, R. A. Holroyd, and M. Nishikawa, *J. Phys. Chem.* **89**:2969 (1985).
4. T. Takagi, H. Teranishi, C. Yokoyama, and S. Takahashi, *Thermochim. Acta* **141**:291 (1989).
5. M. L. McGlashan and I. R. McKinnon, *J. Chem. Thermodyn.* **9**:1205 (1977).
6. A. Kumagai and S. Takahashi, *J. Chem. Thermodyn.* **17**:977 (1985).
7. C. Yokoyama and S. Takahashi, *Int. J. Thermophys.* **10**:35 (1989).

8. J. G. Aston, R. M. Kennedy, and G. H. Messerly, *J. Am. Chem. Soc.* **63**:2343 (1941).
9. R. H. Perry and C. H. Chilton, *Chemical Engineers' Handbook*, 5th ed. (McGraw–Hill, New York, 1973).
10. T. Toriumi, K. Date, and H. Iwasaki, *Bull. Chem. Res. Inst. Tohoku Univ.* **10**:263 (1961).
11. C. F. Spencer and R. P. Danner, *J. Chem. Eng. Data* **17**:236 (1972).
12. R. W. Hankinson and G. H. Thomson, *AIChE J.* **25**:653 (1979).
13. G. Soave, *Chem. Eng. Sci.* **27**:1197 (1972).
14. B. I. Lee and M. G. Kesler, *AIChE J.* **21**:510 (1975).
15. D. Ambrose, *Vapor-Liquid Critical Properties*, Rep. Natl. Phys. Lab. U.K. (1979).
16. R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed. (McGraw–Hill, New York, 1977).
17. R. C. Weast and M. J. Astle, *Handbook of Chemistry and Physics*, 62nd ed. (CRC Press, Boca Raton, Fla., 1982).
18. J. H. Dymond and R. Malhotra, *Int. J. Thermophys.* **8**:541 (1987).
19. N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**:635 (1969).
20. M. B. Ewing and K. N. Marsh, *J. Chem. Thermodyn.* **9**:357 (1977).
21. P. R. Bienkowski and K. C. Chao, *J. Chem. Phys.* **62**:615 (1975).
22. F. Del Rio and D. A. de Longi, *Phys. Lett.* **56A**:463 (1976).
23. I. Nezbeda and K. Aim, *Fluid Phase Equil.* **17**:1 (1984).