Density of water at subzero temperature under high pressure: measurements and correlation

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S Asada[1], T Sotani[2], J Arabas[3], H Kubota[2], S Matsuo[2] and Y Tanaka[2]

[1] Konan Women's University, 6-2-23 Morikita-cho, Higashinada-ku, Kobe 658-0001, Japan
[2] Kobe University, 1-1 Rokkodai-cho, Nada, Kobe 657-8501, Japan
[3] High Pressure Research Centre of the Polish Academy of Sciences, 29/37 Sokolowska St., 01-142 Warsaw, Poland

Abstract
We measured the specific volumes of water at temperatures from 253 to 298 K and at pressures from 200 to 380 MPa. The specific volume data obtained were correlated with an empirical Tait equation as a function of temperature and pressure. In addition to our experimental data, some calculated data from the 'IAPWS-95' equation of state (released by the International Association for the Properties of Water and Steam) were used to enable extrapolation up to 373 K. Compressibility and expansivity were calculated by differentiating this equation.

1. Introduction

As the result of a great deal of effort in the investigation of the thermophysical properties of water, we can utilize many more data in scientific and technological applications than for other liquids. However, there are fewer data on the properties of water under high pressure over 200 MPa. In particular, there is just one report—that of Bridgman [1]—on the volumetric behaviour of water in this region.

We developed an apparatus for making accurate measurements of density of water at subzero temperature under high pressure. Some data obtained at temperatures from 253 to 298 K and pressures up to 200 MPa were reported [2, 3]. In this study, consecutive measurements at pressures from 200 to 380 MPa were carried out. The volumetric data obtained were compared with some experimental data and the equation of state reported previously. The empirical Tait equation was developed on the basis of these data and some data calculated with IAPWS-95 equation of state[4].

[4] The release on the *IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water for General and Scientific use*, from the International Association for the Properties of Water and Steam in 1995.
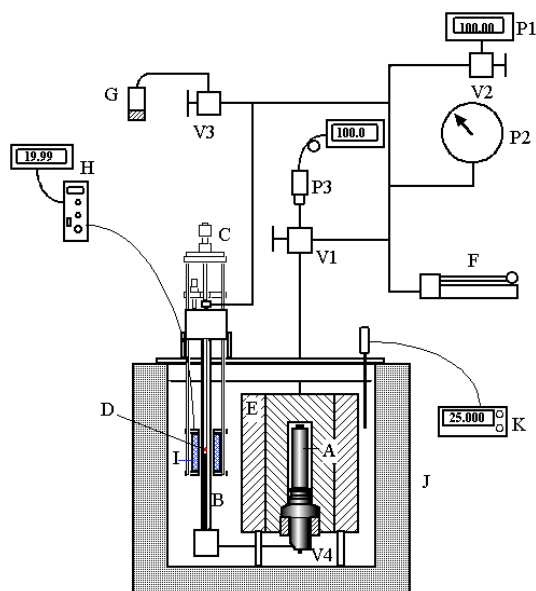
Figure 1. A schematic diagram of the apparatus: A: sample cell; B: high-pressure burette; C: micrometer; D: metal float; E: high-pressure vessel; F: oil pump; G: oil reservoir; H: displacement meter; I: differential transformer; J: constant-temperature bath; K: quartz thermometer; P1, P2: pressure gauges; V1–V4: valves.

2. Experimental details

A detailed description of the apparatus used in this experiment has been reported previously. Figure 1 shows a schematic diagram of the apparatus. The sample was separated by mercury from the pressure-transmitting fluid. In this method, the volume change of the sample under pressure, ΔV_{app}, was calculated from the meniscus displacement of the mercury used as the liquid piston in the burette and the cross-sectional area of the burette. The specific volume, v_{sp}, was calculated using the following relation:

$$v_{sp} = v_{sp}^0 - \frac{\Delta V_{app} - \Delta V}{W} \tag{1}$$

where W is the sample mass and v_{sp}^0 is the specific volume at the initial conditions. In this case, the specific volume at 298.15 K and atmospheric pressure calculated from the equation of state was used as v_{sp}^0. ΔV is the correction term for the volume change due to both compression of mercury and the deformation of the burette, the connecting tube, and the sample cell under pressure. The differential transformer equipped with the burette was employed for the detection of the meniscus of mercury. The final uncertainties in the specific volume measurement are estimated to be less than ±0.1%. The measurements were carried out at temperatures from 253 to 298 K and at pressures from 200 to 380 MPa.

3. Results and discussion

3.1. Comparison of experimental data

To confirm the reliability of the measurements, the data obtained at 298.15 and 273.15 K were compared with previous works [1, 3, 5–7]. As shown in figure 2, the data agree with the values calculated from the following accurate equation of state within ±0.06%.
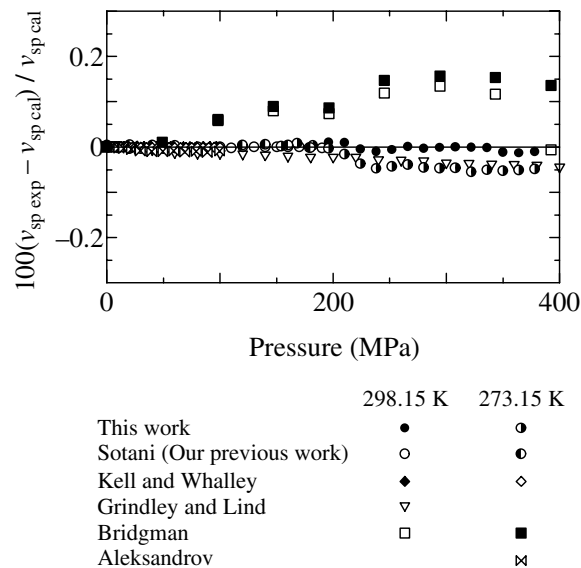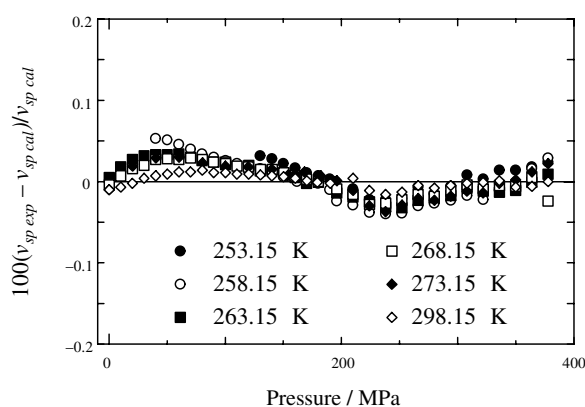
Figure 2. Comparison of the specific volumes obtained at 298.15 and 273.15 K.
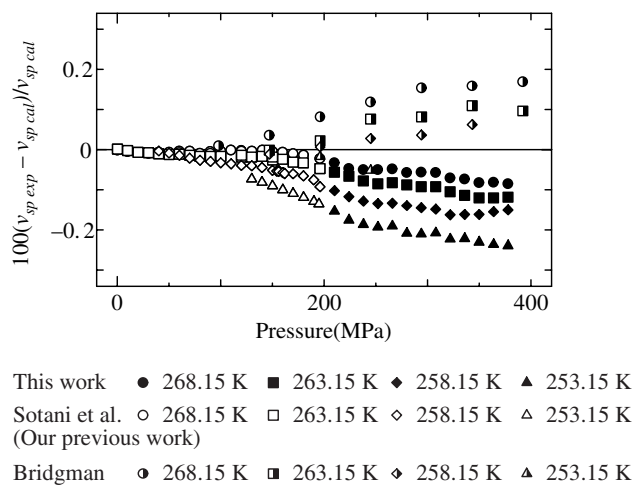
Figure 3. Comparison of the specific volumes obtained at subzero temperature with the literature data.

The International Association for the Properties of Water and Steam released the formulation (IAPWS-95) for general and scientific use in 1995. IAPWS-95 is an equation of state based on the Helmholtz function and applicable over a wide temperature and pressure range. The specific volumes obtained are shown in figure 3 as relative deviations from IAPWS-95 values. Our data below 100 MPa agree with the values calculated from IAPWS-95 within $\pm 0.05\%$. On the other hand, some systematic discrepancies between our data and IAPWS-95 data were observed above 200 MPa. Their extent increased with dropping temperature. The estimated uncertainties in density calculated using IAPWS-95 in this region are reported to be less than $\pm 0.2\%$. Our data, except some data at 253 K, agree with the estimated uncertainties of $\pm 0.2\%$. IAPWS-95 is a revision of the equation of state [4] proposed by Saul and Wagner

Figure 4. The relative deviation from the Tait equation (2) of the specific volumes obtained.

Table 1. Coefficients in equations (2)–(5).

i	a_i	b_i	c_i
0	$8.473\,542 \times 10^1$	$-1.342\,996 \times 10^4$	$-5.910\,172 \times 10^0$
1	$-1.585\,480 \times 10^0$	$1.519\,385 \times 10^2$	$7.350\,484 \times 10^{-2}$
2	$1.251\,567 \times 10^{-2}$	$-6.404\,284 \times 10^{-1}$	$-3.370\,865 \times 10^{-4}$
3	$-5.268\,972 \times 10^{-5}$	$1.225\,469 \times 10^{-3}$	$6.907\,013 \times 10^{-7}$
4	$1.246\,782 \times 10^{-7}$	$-9.033\,103 \times 10^{-7}$	$-5.335\,347 \times 10^{-10}$
5	$-1.571\,246 \times 10^{-10}$		
6	$-8.236\,444 \times 10^{-14}$		

in 1989. In comparison with the Saul–Wagner equation of state, our data show smaller and more positive deviations. Although these formulations were developed on the basis of many estimated thermophysical data, Bridgman's data were adopted as the unique density data for the low-temperature region under high pressure over 200 MPa. Our data would be useful for developing a formulation such as IAPWS-95.

3.2. Correlation of experimental data

We tried to correlate the volumetric data as a function of temperature and pressure. To represent the anomalous behaviour in both thermal expansivity and isothermal compressibility of water around 323 K, our experimental data and some data calculated using IAPWS-95 at temperatures from 303 to 373 K and pressures up to 380 MPa were used. The correlation of these data was carried out using the empirical Tait equation:
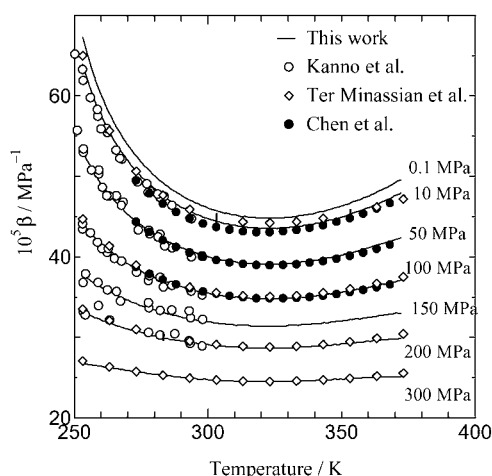
$$v(T, p) = v_0(T)\left[1 - C(T)\ln\left(\frac{B(T) + p}{B(T) + p_0}\right)\right] \tag{2}$$

$$v_0(T) = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4 + a_5T^5 + a_6T^6 \tag{3}$$

$$B(T) = b_0 + b_1T + b_2T^2 + b_3T^3 + b_4T^4 \tag{4}$$

$$C(T) = c_0 + c_1T + c_2T^2 + c_3T^3 + c_4T^4 \tag{5}$$

where v_0 is the specific volume at atmospheric pressure ($p_0 = 0.101\,325$ MPa) and fitted to a sixth-order polynomial in temperature. The terms of both $B(T)$ and $C(T)$ can be represented by fourth-order polynomials in temperature. T is the temperature in kelvins and P is the

Figure 5. Isothermal compressibility calculated from the Tait equation (2) together with literature data.
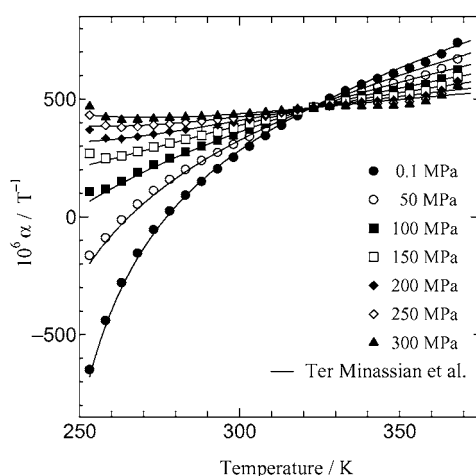
Figure 6. Thermal expansivity calculated from the Tait equation (2) together with literature data.

pressure in megapascals. This equation is applicable in the temperature range from 253 and 298 K and at pressures up to 380 MPa, including the measured supercooled region. The values of each of the coefficients are listed in table 1. This equation can reproduce all the data used for the correlation within maximum deviation of $\pm 0.06\%$. Figure 4 shows the relative deviation of the specific volume obtained in this study from this equation.

Isothermal compressibility and thermal expansivity can be obtained by differentiating equation (2) with respect to pressure and temperature, respectively:

$$\beta = -(1/v)(\partial v/\partial P)_p, \qquad \alpha = (1/v)(\partial v/\partial T)_P.$$

Figure 5 shows a comparison of the isothermal compressibility obtained in this study with the literature data [8–10]. These measurements were carried out with the capillary method and piezothermal method. Our calculated value shows good agreement.

Figure 6 shows a comparison of the thermal expansivity obtained in this study with the literature data. The full curve was calculated with the equation reported by Ter Minassian and

Pruzan in 1981. Our thermal expansivity value below 323 K shows good agreement without a defective curvature appearing around 343 K.

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