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Received for review July 1, 1985. Accepted November 6, 1985. We gratefully acknowledge the support of the Ministero Pubblica Istruzione of Italy.

An Empirical Equation of State for Pure Water in the Oceanographic Region of Temperature and Pressure Determined from Direct Measurements†

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Polynomial regression fits to the results of measurements on distilled water of the thermal expansion at a number of pressures and of the compression at a single temperature are combined to form an empirical equation of state which is valid in the ranges $T \leq$ 0–30 °C and atmospheric pressure to 1000 bars. The specific volume from the equation has a standard error of 3×10^{-6} cm^3/g or better over the entire region and its inaccuracy is estimated to be not worse than 25×10^{-6} cm^3/g at 1000 bars. The measurements are direct volumetric ones which are based on calibrations using mercury $P-V-T$ data. The equation of state for water presented agrees within 20×10^{-6} cm^3/g with two recent equations derived from sound speed measurements. Some properties derived from the equation are compared with those found by others.

The results of direct measurements of the volume properties of pure water in the oceanographic region of temperature and pressure are presented here. They are summarized as an empirical equation of state using polynomial least-squares fits. The data on which they are based was part of our contribution to the data set used in the formulation of an empirical equation of state for seawater (*1*) which has been endorsed by the UNESCO Joint Panel on Oceanographic Tables and Standards. The remaining pure water data used in that data set was that from Chen, Fine, and Millero's (*2*) equation of state for water, determined from Wilson's (*3*) sound speed data, for the 0–100 °C, atmospheric pressure to 1000 bar region. Our pure water data consist of compressions to 1000 bars at 10 °C IPTS-48 and isopiestic thermal expansions in the temperature range $T \leq$ 0–30 °C at pressures up to ~1000 bars. The compression data was published earlier (*4*), but the thermal expansion data has not been published before. The water data is important not only as a necessary component in the formulation of a seawater equation which goes to zero salt concentration but also by itself, because an accurate water equation can be used in calibrations of instruments for future measurements of the $P-V-T$ relations in seawater and other aqueous solutions. Our measurements, in particular, have value because they provide, within the experimental differences between the two, a confirmation of the sound speed based results by a direct volumetric method and because they yield specific volumes below 0 °C, where the temperatures of maximum density lie at higher pressures.

Kell and Whalley (*5*) also determined precisely the $P-V-T$ properties of water by direct volumetric measurement to 1000 bars over a much larger temperature range, 0–150 °C. There are differences, however, of over 100 ppm of the specific volume at 1000 bars between their values and those determined from Wilson's (*3*) sound speeds; this was pointed out by Fine and Millero (*6*) from results of their determination of compressions from sound speeds. Later, more accurate determinations of compressions from sound speeds by Kell and Whalley (*7*) and by Chen, Fine, and Millero confirmed this, as do our own results from direct measurements.

Experimental Section

Apparatus and Procedures. The apparatus and the experimental and data workup procedures used for our measurements on water were described in detail earlier (*4*, *8*, *9*). The change in sample volume with temperature or with pressure was measured in a dilatometer, by which means the change can be measured to a high resolution from the change in length in a small-diameter, precision-bore tubing whose volume is continuous with that of the main sample volume. Two different fused-quartz dilatometers were used, one for the thermal expansion and one for the compression measurements. In the thermal expansion and compression determinations a 1 ppm change in the sample volume (~45 cm^3) corresponded to ~14 and ~2 μm, respectively, change in length along the dilatometer capillary. The sample was separated from the pressure transmitting fluid (distilled water) in the pressure vessel which enclosed the dilatometer by mercury, which extended from the bottom of the main volume of the dilatometer up into the measuring section of the precision-bore capillary. The height of the mercury in the measuring section was followed by measuring the position of a small, magnetic-steel cylinder

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† W.H.O.I. Contribution No. 5898.

0021-9568/86/1731-0189$01.50/0

Table I. Compression of Water Data at 9.9957 °C (IPTS-68)

abs press., bar	sample vol, cm^3
7.38	43.208 09
10.83	43.200 95
17.72	43.186 77
201.30	42.819 79
401.05	42.443 27
600.79	42.088 25
800.52	41.753 63
1000.19	41.437 09

floating on the mercury column with a differential transformer which was coupled to a precision micrometer. Pressure was measured by a dead-weight piston gauge (see below) and temperature was obtained from the temperature of the constant temperature bath in which the pressure vessel was immersed using a G-2 Mueller bridge–platinum resistance thermometer combination.

The distilled water used in the measurements was double-distilled Woods Hole tap water having an electrical conductivity of about 1×10^{-6} $(\text{ohm cm})^{-1}$. It was partially degassed by stirring under vacuum before transfer to the dilatometer.

Calibrations. The volumes of the dilatometers in the pressure and temperature ranges of the measurements were determined by calibration against mercury (*4*, *8*). The values of the specific volume of mercury used were obtained from the correlating equation of Bett, Weale, and Newitt (*10*). The volume expansion of the calibrated thermal expansion dilatometer for the temperature change 0–40 °C at atmospheric pressure differed by $3^1/_2$ ppm of the volume from that derived from the equation of Beattie et al. (*11*) for the linear thermal expansion of vitreous silica. The volume compression of the compression dilatometer at 1000 bars and 20 °C agreed within ~30 ppm of the volume with the value derived from the equation of Reitzel, Simon, and Walker (*12*) for the linear compression of vitreous silica.

The dead-weight (simple) piston gauge (Aminco Model 47-12215) used for the water thermal expansion measurements was a different unit from the one (Aminco Model 47-2221) used for the earlier compression (*4*) and the earlier seawater thermal expansion measurements (*8*), but was identical in the gauge piston–cylinder design; measurements of the compression of ~35 ‰ salinity seawater at 10 °C IPTS-48 and 1000 bars using the two gauges agreed within the precision of the measurements (standard deviation of a single observation ≈ 2×10^{-6} of the volume, or 0.005% of the compression) (*9*), which confirmed earlier cross-floating comparisons between the two gauges. The gauge used for the water thermal expansion measurements was calibrated at several pressures against a Harwood Engineering Co. controlled-clearance gauge and was found to differ from that gauge by 0.35 bars at 1000 bars; all pressures given in this paper are based on this calibration, which has been applied to both dead-weight gauges and which is believed to be accurate to about 0.01% of the pressure at 1000 bars.

Compression Data

The observed volume vs. pressure data for water at 9.9957 °C IPTS-68 (=10 °C IPTS-48) is given in Table I. It was obtained from the data given in Table 1A of our paper on the compressibility of distilled water and seawater (*4*) after correcting the pressures given there according to the above pressure gauge calibration and correcting trivial errors in the volumes at 200 and 1000 bars. The first and final volume measurements in the original data set were omitted for the reasons given in that paper. A third-degree polynomial regression of volume on pressure was chosen to be the best fit to the selected data based on F tests at the 5% level of significance. The standard deviation for a single observation from this polynomial was 1.9 ppm of the volume. The sample volume at atmospheric pressure (1.01 bars) was estimated from the polynomial regression, and observed specific volume compressions were computed from the volumes in Table I by using Kell's (*13*) value for the density of water at 9.9957 °C and atmospheric pressure. These compressions are given in Table II. The regression of specific volume compression, $C(P,T)$, on applied pressure (absolute minus atmospheric) is given by

Table II. Observed Values of Compression of Water at 9.9957 °C (IPTS-68), Expressed as Specific Volume Change

applied press., bar	sp vol compression, 10^{-6} cm^3/g
6.37	303.8
9.82	469.1
16.71	797.2
200.29	9290.5
400.04	18004.6
599.78	26221.1
799.51	33965.4
999.18	41291.3

Table III. Values of Coefficients in Compression and in Thermal Expansion Polynomials in the Equation of State (Eq 4)[a]

Compression Polynomial $C(p, 9.9957)$

$a_1 = 4.7822114 \times 10^{-5}$
$a_2 = -7.371269 \times 10^{-9}$
$a_3 = 8.69464 \times 10^{-13}$

Thermal Expansion Polynomial $E(P, T)$

i	j	$10^6 b_{ij}$[b]	i	j	$10^6 b_{ij}$[b]
0	1	−6.752559E+1	1	5	1.068546E−8
0	2	9.069789	2	1	−1.2996885E−4
0	3	−1.0166528E−1	2	2	4.065389E−6
0	4	1.270891E−3	2	3	−6.487625E−8
0	5	−8.68175E−6	2	4	4.92114E−10
1	1	3.9093628E−1	3	1	1.064121E−8
1	2	−9.543167E−3	3	2	−6.90740E−10
1	3	1.4900218E−4	3	3	8.90553E−12
1	4	−1.826021E−6	4	1	3.145838E−12

[a] A check value for $v(P, T)$ from our equation of state using these coefficients and $v(0,9.9957) = 1.000\,300\,1$ is $v(1000,30) = 0.965\,220\,1$. [b] E±n stands for $\times 10^{\pm n}$.

$$C(P,9.9957) = v(0,9.9957) - v(P,9.9957) = a_1P + a_2P^2 + a_3P^3 \quad (1)$$

where $v(P,T)$ is the specific volume in cm^3/g at P bars applied pressure and T °C is on the IPTS-68 temperature scale. The values of the coefficients are given in Table III.

Expansion Data

The observed thermal expansions, expressed as specific volume change, from 0 °C to T in the interval $T \leq$ 0–30 °C (IPTS-68) at 7–980 bars applied pressure are given in Table IV, sections A and B. The maximum standard deviation for a single observation at each of the measurement pressures found by polynomial regression analysis was not greater than 0.5×10^{-6} cm^3/g. Regression polynomials in P and T of the form

$$v(P,T) - v(P,0) = b_{00} + (b_{10}P + b_{01}T) + (b_{20}P^2 + b_{11}PT + b_{02}T^2) + \ldots + \left(\sum_{i=0,j=n-i}^{n} b_{ji} P^j T^i\right) \quad (2)$$

where the units of $v(P,T)$ are cm^3/g, were fitted to the data. F tests were used to test the significance of terms at the 5% level. In a fit of the 7th degree the 7th degree term ($n = 7$) in P and T was not significant but the 6th degree term was. In the 6th degree term b_{06} and b_{42} were not significant and were dropped. The unbiased estimate of the standard deviation of a single observation of $v(P,T) - v(P,0)$ from the resulting fit

Table IV. Observed Values of Thermal Expansion of Water Referred to 0 °C (IPTS-68), Expressed as Specific Volume Change (10^{-6} cm^3/g)

A

	applied pressure, bar					
temp, °C	7.32	100.31	200.21	300.11	400.00	499.89
30	4254.4	4788.2	5338.5	5849.9	6330.8	6782.2
29						
28	3662.6	4183.6	4718.9	5216.8	5685.8	6124.4
26	3108.3	3613.4	4132.4	4614.5	5067.6	5493.1
24	2591.3	3077.6	3578.4	4042.8	4478.9	4887.3
22	2112.6	2578.7	3058.0	3502.4	3919.9	4309.0
20	1675.8	2118.6	2572.6	2993.9	3391.2	3758.6
18	1281.5	1698.2	2123.1	2519.4	2891.9	3237.2
16	931.3	1318.3	1712.7	2080.6	2424.3	2744.5
14	626.4	981.3	1341.1	1677.1	1991.0	2282.2
12	370.0	688.0	1010.8	1311.3	1592.0	1851.6
10	165.0	441.9	722.6	984.0	1228.4	1453.8
8	11.9	243.9	478.8	697.8	902.0	1089.8
6	−84.3	98.0	282.2	453.6	614.0	761.4
4	−121.0	6.3	135.3	254.7	366.3	469.1
2	−94.0	−27.1	40.4	102.4	161.1	214.7
0	0.0	0.0	0.0	0.0	0.0	0.0
−1			2.2	−31.5		
−2					−113.6	−172.6
−4						

B

	applied pressure, bar					
temp, °C	599.76	699.60	799.49	913.14	978.56	978.54
30	7200.9	7588.4	7953.2	8325.4	8529.1	
29						8172.4
28	6531.2	6908.9	7262.8	7624.6	7821.7	7821.7
26	5886.5	6251.3	6592.8	6942.8	7133.8	7133.0
24	5266.3	5616.8	5945.1	6280.6	6463.3	6463.3
22	4670.7	5005.4	5318.5	5638.2	5812.5	5811.4
20	4101.4	4418.3	4713.2	5016.5	5181.3	5180.9
18	3558.6	3854.9	4131.0	4414.6	4569.3	4568.0
16	3042.8	3316.4	3571.7	3834.1	3977.0	3976.7
14	2554.9	2803.7	3036.8	3274.6	3405.0	3405.0
12	2094.2	2317.0	2524.9	2737.3	2852.9	2852.9
10	1664.5	1857.9	2037.3	2222.6	2322.3	2322.2
8	1265.8	1427.2	1576.7	1729.7	1813.1	1812.5
6	898.7	1025.1	1142.1	1260.8	1325.8	1325.8
4	564.4	652.3	733.6	815.7	860.7	860.7
2	264.8	309.6	352.9	394.9	419.1	418.6
0	0.0	0.0	0.0	0.0	0.0	0.0
−1						
−2	−226.7	−276.7	−322.1	−369.7	−395.0	−394.7
−4	−414.5	−518.4	−614.0	−713.2	−765.4	−765.5

was 0.78 × 10^{-6} cm^3/g with 183 degrees of freedom.

By rearrangement of terms the above fit can be written as

$$v(P,T) - v(P,0) = b_{01}T + b_{02}T^2 + b_{03}T^3 + b_{04}T^4 + b_{05}T^5 + (b_{11}T + b_{12}T^2 + b_{13}T^3 + b_{14}T^4 + b_{15}T^5)P + (b_{21}T + b_{22}T^2 + b_{23}T^3 + b_{24}T^4)P^2 + (b_{31}T + b_{32}T^2 + b_{33}T^3)P^3 + b_{41}TP^4 + f(P) \quad (3)$$

where $f(P)$ is a 6th degree polynomial in P. $f(P)$ is the intersection of the regression surface with the $T = 0$ plane; at each of the pressures P_m of the thermal expansion measurements it gives the intercept of the estimate at the experimental point (P_m, 0). Its absolute value over the pressure range was less than 1 × 10^{-6} cm^3/g. To make $E(P,T) = v(P,T) - v(P,0) = 0$ at $T = 0$, $f(P)$ is dropped to give the estimate for the specific volume thermal expansion from 0 to T °C. The values of the coefficients in the estimate $E(P,T)$ are given in Table III.

Equation of State

The equation of state for water is given by

$$v(P,T) = v(0,9.9957) - C(P,9.9957) + E(P,T) - E(P,9.9957) \quad (4)$$

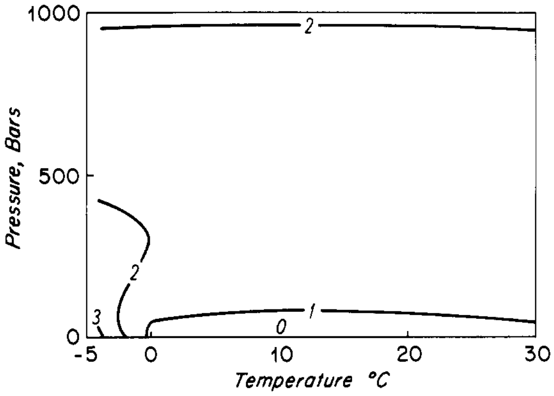

Figure 1. Standard error of specific volume (10^{-6} cm^3/g) for our equation of state.

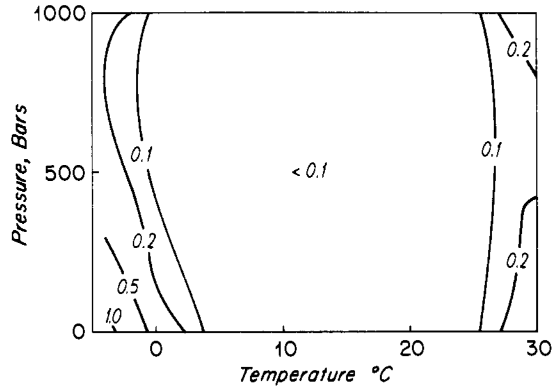

Figure 2. Standard error of dv/dT (10^{-6} cm^3/°C) for our equation of state.

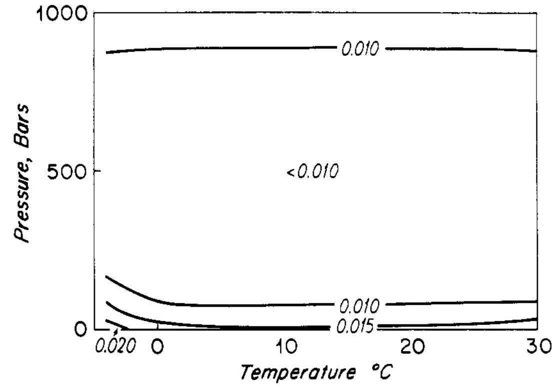

Figure 3. Standard error of dv/dP (10^{-6} cm^3/bar) for our equation of state.

We computed $v(0,9.9957)$ = 1.000 300 1 cm^3/g from Kell's (*13*) formula for the density of water at atmospheric pressure.

Because the random errors of the compression and the thermal expansion measurements are independent, the standard errors (σ) of v, dv/dt, and dv/dP can be estimated, assuming $\sigma[v(0,9.9957)] = 0$, from

$$\sigma^2[v(P,T)] = \sigma^2[C(P,9.9957)] + \sigma^2[E(P,T) - E(P,9.9957)] \quad (5)$$

$$\sigma^2[\mathrm{d}v/\mathrm{d}T] = \sigma^2[\mathrm{d}E(P,T)/\mathrm{d}T] \quad (6)$$

$$\sigma^2[\mathrm{d}v/\mathrm{d}P] = \sigma^2[\mathrm{d}C(P,9.9957)/\mathrm{d}P] + \sigma^2[\mathrm{d}E(P,T)/\mathrm{d}P - \mathrm{d}E(P,9.9957)/\mathrm{d}P] \quad (7)$$

using the variances and covariances of the coefficients in $C(P,T)$ and $E(P,T)$. The latter are found from the variances of the residuals and the coefficients in the inverse matrix found

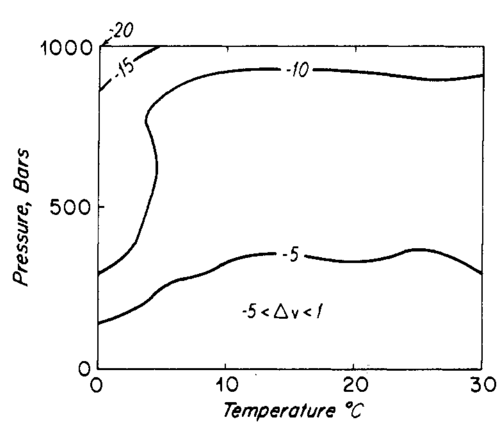

Figure 4. Comparison of our equation of state with that of Chen, Fine, and Millero (*2*), our values minus theirs (Δv). Units: 10^{-6} cm^3/g; at atmospheric pressure, $-3 < \Delta v < 1$; at 1000 bars, $-21 < \Delta v < -12$.

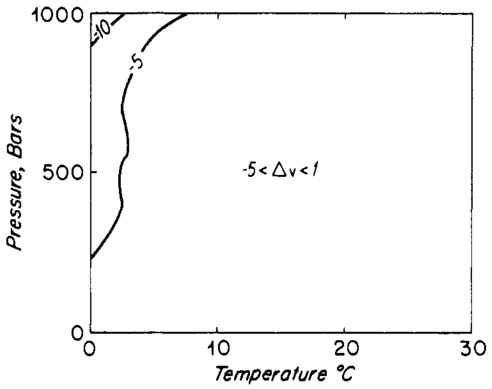

Figure 5. Comparison of our equation of state with that of Kell and Whalley (*7*), ours values minus theirs (Δv). Units: 10^{-6} cm^3/g; at an absolute pressure of 1 bar, $-3 < \Delta v < 0$; at 1000 bars, $-15 < \Delta v < -1$.

in the solution of the normal equations in both cases [see Bradshaw (*14*)]. These errors are contoured in Figures 1–3.

The accuracy of the specific volumes given by our equation of state depends principally on the accuracy of Bett, Weale, and Newitt's mercury $P-V-T$ equation and on the accuracy of our pressure gauge. Davis and Gordon (*15*) determined the volume of mercury as a function of pressure by ultrasonic velocity measurements at 21.9, 40.5, and 52.9 °C. Their accuracy estimates yield a value of better than 10 ppm of the volume for the compression at 1000 bars. Compressions computed from Bett, Weale, and Newitt at 1000 bars agree to within 10 ppm of the volume with those of Davis and Gordon at the three temperatures. (In an earlier paper (*8*) we had erroneously estimated the disagreement at 21.9 °C at about 60 ppm of the volume.) Our estimated accuracy of 0.01% at 1000 bars for our pressure gauge corresponds to 4 ppm of the volume of water. These results suggest that the inaccuracy in our specific volume data is probably not worse than 25×10^{-6} cm^3/g at 1000 bars.

Comparisons

Equations of State. Our equation of state agrees slightly better with that of Kell and Whalley (*7*) than with that of Chen, Fine, and Millero (*2*), as shown in Figures 4 and 5. The reasons for the differences between the two latter equations, both based on the same sound speed data and both using Kell's (*13*) densities and de Haas' (*16*) specific heat data at atmospheric pressure, are, presumably, the different sound speed data treatments and the different methods of determining compressions from sound speeds using the sound speed differential equation. It should be noted that, in addition to Wilson's data, both groups used Del Grosso's (*17*) and Del Grosso and Mader's (*18*) sound speed data at atmospheric pressure. This was to correct Wilson's data, which was not believed to be the most reliable at that pressure. The principle used in making this correction was to assume that the error found at atmospheric pressure had the same value in the data at higher pressures and the same temperature.

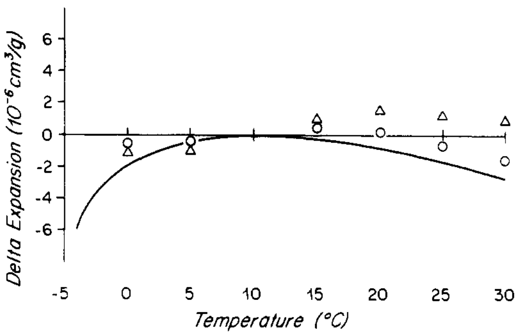

Figure 6. Comparison of our thermal expansions, in terms of specific volume change and with reference to 10 °C, and those of Bigg (*25*) at atmospheric pressure with those of Kell (*13*): ours minus Kell (—); Bigg minus Kell assuming Bigg temperature scale is (1) IPTS-48 (Δ) and (2) IPTS-68 (O).

Kell and Whalley also derived equation of state results from Barlow and Yazgan's (*19*) high-pressure sound speed data by their method. The above equations of state using Wilson's data are for the region up to 1000 bars for 0–100 °C; that derived from Barlow and Yazgan's data does not go below 15 °C or above 800 bars. Our agreement with the specific volumes based on Barlow and Yazgan's sound speed measurements is not quite as good as with the two using Wilson's data: at 800 bars the differences go from -11×10^{-6} to -20×10^{-6} cm^3/g in going from 15 to 30 °C.

As mentioned above, Kell and Whalley's direct volumetric measurements of compression (*5*) do not agree with those derived from Wilson's sound speeds. They give values for the specific volume of water at 1000 bars which are too low compared with those based on sound speeds [the above and others (*6*, *20*, *21*)] by as much as ~100 ppm of the volume; the present direct volumetric measurements, which use the same values for the specific volume of mercury for the volume calibration as used by Kell and Whalley, support the sound speed results.

Thermal Expansions at Atmospheric Pressure. Thermal expansion results from our equation of state at atmospheric pressure depend mainly on Sears' (*22*) formula for the volume thermal expansion of mercury at atmospheric pressure, which was used by Bett, Weale, and Newitt. For comparison, Beattie et al.'s (*11*) formula gives a value for the volume thermal expansion of mercury from 0 to 30 °C which is 1.9 ppm of the volume lower than that given by Sears' formula.

We compare our thermal expansions, expressed as specific volume changes and referred to 10 °C, at atmospheric pressure with those derived from Kell's densities in Figure 6. Because our thermal expansions at higher pressures extend to −4 °C, we have calculated values to this temperature, in the metastable liquid water region at atmospheric pressure, for comparison with Kell's extrapolated values. Kell's densities in the 0–40 °C range are based on and are, for practical purposes, the same as those given by Tilton and Taylor's (*23*) formulation of the data of Chappuis (*24*), after conversion from the IPTS-27 (=IPTS-48) temperature scale assumed by Tilton and Taylor for these early measurements to the IPTS-68 scale.

Bigg (*25*) derived densities for the range 0–40 °C from an analysis of the measurements of both Chappuis and Thiesen, Scheel, and Diesselhorst (*26*) and, like Kell, he assumed that these early measurements were on the IPTS-48 scale. Com-

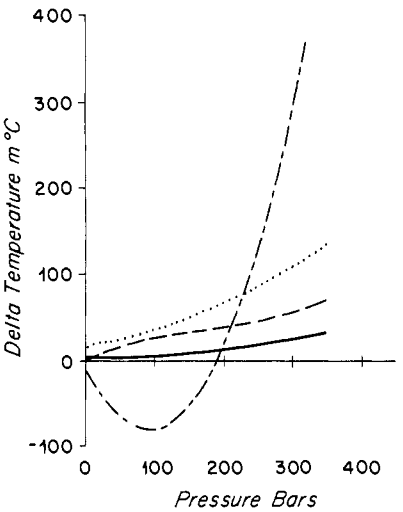

Figure 7. Comparison of temperatures of maximum density [$(dv/dT)_p$ = 0)], theirs minus ours: ---, Zaworski and Keenan (*29*); ···, Chen, Fine, and Millero (*2*); — — —, Caldwell (*27*); —, our standard error.

Table V. Temperatures of Maximum Density Calculated from Equation of State

appl press., bar	temp of max density, °C (IPTS-68)	std error, °C
0	3.971	0.006
100	1.877	0.006
200	−0.38	0.01
300	−2.81	0.02
400	−5.44	0.04
500	−8.3	0.1
600	−11.5	0.1
700	−15.1	0.2

parisons of thermal expansions from his results with those from Kell are also shown in Figure 6.

There is an uncertainty as to which of the modern scales is closest to the one in use at the time of the early measurements (*13*). In order to show the effect of assuming the IPTS-68 scale for these measurements, we also show the Bigg comparison assuming this temperature scale for his densities in Figure 6. This slightly improves the general agreement between his and our expansions, as it would in our comparison with Kell if the latter had assumed the IPTS-68 scale for the early measurements.

Temperatures of Maximum Density. In Figure 7 the temperatures T_{max} at which $(dv/dT)_p = 0$ as a function of pressure are compared with those derived from the Chen, Fine, and Millero equation of state and with those from our quadratic regression on pressure of the directly measured *water* values of Caldwell (*27*). (Caldwell actually determined the pressure at which the adiabatic temperature change with pressure was zero at each of his T_{max} temperatures.) Values given in Dorsey (*28*), based on much earlier measurements, were summarized by Zaworski and Keenan (*29*); their fit is also compared with our results in Figure 7. Finally, the estimated standard errors (σ) for our values are shown. Our values for T_{max} agree best with Caldwell's. We calculated the standard error of our fit to his water results, and found it to be 11 m °C at atmospheric pressure and to lie between 7 and 13 m °C at elevated pressures. At all pressures the differences between his and our values are within 2.3 times the standard error of the difference. Our disagreement with Chen, Fine, and Millero is greater than with Caldwell over the entire pressure range. This disagreement might not be significant, of course, if their standard errors (unknown) were taken into account. In Table V we give our values for T_{max} and its standard error for pressures up to 700 bars. At the higher pressures the values are extrapolated beyond the temperature range of the thermal expansions at those pressures. At 800 bars and above the standard errors of T_{max} exceed 0.5 °C.

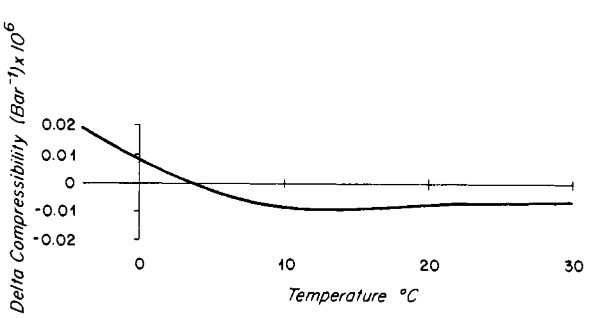

Figure 8. Comparison of our isothermal compressibilities at atmospheric pressure with those of Kell (*13*), ours minus his.

At atmospheric pressure we find a value of 3.971 °C, σ = 0.006, for the temperature of maximum density and a value of −0.0202 °C/bar, σ = 0.0002, for the change of the temperature of maximum density with pressure. (Based on the difference in mercury thermal expansion coefficients [0.03 ppm/°C] between the formulas of Sears and of Beattie et al. at 4 °C we would obtain T_{max} = 3.973 °C if we substituted Beattie et al.'s for Sears' formula in Bett, Weale, and Newitt's *P*−*V*−*T* equation for mercury.) Kell (*13*) found 3.983 °C and −0.0200 °C/bar, with an estimated uncertainty of 0.0002 in the latter, for the same quantities. The quadratic regression of Caldwell's T_{max} on pressure for his pure water data alone gives T_{max} = 3.971 °C, σ = 0.011, and dT_{max}/dP = −0.0198 °C/bar; Chen, Fine, and Millero's equation of state, which uses Kell's (*13*) densities at atmospheric pressure, yields a value of 3.985 °C for T_{max}.

Isothermal Compressibilities at Atmospheric Pressure. In Figure 8 we compare our isothermal compressibilities at atmospheric pressure with those obtained by Kell (*13*) using the sound speed data of Del Grosso and Del Grosso and Mader. Referring to Figure 3 for our standard error for *dv*/*dP* at atmospheric pressure, we are in good agreement with the more precise values of Kell.

Summary

An equation of state for water in the region $T \leq$ 0–30 °C and atmospheric pressure to 1000 bars based on direct volumetric measurements has been given. It is in good agreement with two recent ones derived by using the sound speed data of Wilson and of Del Grosso and Del Grosso and Mader. The thermal expansions, in terms of specific volume change, derived from it at atmospheric pressure and with reference to 10 °C, agree to within 3 × 10^{-6} and 4 × 10^{-6} cm^3/g with those calculated from Kell's and from Bigg's densities; the agreement is improved if the IPTS-68 temperature scale is assumed for the early measurements on which the latter densities are based. The isothermal compressibilities at atmospheric pressure are in good accord with the precise values of Kell (*13*). We agree fairly well with the temperatures of maximum density of Caldwell.

Acknowledgment

We thank N. P. Fofonoff for his helpful criticisms of the manuscript.

Registry No. H_2O, 7732-18-5.

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Received for review August 1, 1985. Accepted November 22, 1985. Research supported by the Oceanographic Section of the National Science Foundation (OCE74-18158).

Room Temperature Fused Salts Based on Copper(I) Chloride–1-Methyl-3-ethylimidazolium Chloride Mixtures. 1. Physical Properties

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Mixtures of CuCl and 1-methyl-3-ethylimidazolium chloride form room temperature ionic liquids over the composition range 0.33 < mole fraction CuCl χ < 0.67, with glass transition temperatures of about −50 °C. Densities, viscosities, and specific conductivites are reported in the range 25–50 °C. Density increases monotonically with χ. Viscosity η goes through a pronounced minimum and specific conductivity κ a pronounced maximum at χ = 0.5; these properties have more desirable values than for the previously studied CuCl–triethylammonium chloride fused salt. Activation energies for viscous flow and for specific and equivalent conductivity are calculated. The Frenkel function $\kappa^{E_{\eta}\dagger/E_{\kappa}\dagger}(\eta)$ = constant is obeyed.

Introduction

Room temperature fused salts containing chlorocuprate(I) anions have been described with various trialkylammonium and with triethylphosphonium and triethylchlorophosphonium cations. The density, conductivity, and viscosity of the prototype of these copper-based liquids, triethylammonium dichlorocuprate(I), have been reported over a range of temperatures (*1*). That compound was used in electrochemical studies of the copper(II,I) and copper(I,0) couples (*1*). Practical application, e.g., in batteries, is limited by its excessively high viscosity and by the excessively low exchange current densities of the above couples.

An important recent advance in the study of low-melting chloroaluminate electrolytes was the development by Wilkes and co-workers of the 1,3-dialkylimidazolium chloride–aluminum chloride melts. The 1-methyl-3-ethylimidazolium system was found to have favorable conductivity and viscosity behavior and a wide liquid range (*2*). This has prompted us to investigate the copper(I) chloride–1-methyl-3-ethylimidazolium chloride (MeEtImCl) system to see if low-melting ionic liquids with more desirable physical and electrochemical properties could be obtained for chlorocuprates. If so, the combination of chloroaluminate and chlorocuprate systems in batteries might prove useful.

Experimental Section

Materials. Copper(I) chloride was prepared by the method of Keller and Wycoff (*3*). 1-Methyl-3-ethylimidazolium chloride was prepared and purified as described by Wilkes and coworkers (*4*); its density as a solid at 21.5 °C was determined by flotation in carbon tetrachloride/hexane to be 1.186 g/mL. The dried chlorides were stored and their mixtures were prepared and transferred in a dry nitrogen-filled glovebox which has been described previously (*1*).

Melting Points. Samples were in sealed glass capillaries under nitrogen. Measurements below room temperature were made by a visual method which has been shown (*2*) to be in agreement with the differential scanning calorimetric technique. The sample capillary and an iron–constantan thermocuple were immersed in ethanol in a small tube which was suspended from the bottom of a rubber stopper in a 400-mL vessel. This vessel was swept with dry nitrogen which first passed through a copper coil immersed in liquid nitrogen; temperature control was achieved by varying the rate of flow of gas. The vessel was mounted in an insulated jacket with a port permitting illumination and observation with a magnifier. Glass transitions were characterized by a discontinuous increase in viscosity on cooling, with fracturing of the melt. The transition temperatures were actually measured as melting points on slow warming after initial quenching to −100 °C. Measurements above room temperature were made using a conventional melting point apparatus.

Other Physical Measurements. Densities of CuCl/MeEtImCl melts were measured by a dilatometric method as previously described (*1*). Viscosities were measured by using a modified Cannon-Fenske viscosimeter whose calibration has been described (*1*). For conductivity measurements, an Industrial Instruments RC16 B2 bridge and a cell of constant 11.65 ± 0.07 cm^{-1} were used. Measurements at 60 and 1000 Hz agreed

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