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Thermodynamic properties of standard seawater

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Abstract

(p, ρ, T) data of standard seawater with practical salinity $S{\approx}35$ (corresponding to an absolute salinity $S_A{\approx}35.16504$ g/kg) measured at T=(273.14 to 468.06) K and pressures up to p=140 MPa are reported with an estimated experimental relative combined standard uncertainty of 0.006% in density. The measurements were made with a newly constructed vibration-tube densimeter. The system was calibrated using double-distilled water, methanol and aqueous NaCl solutions. An empirical correlation for the density of standard seawater has been developed as a function of pressure and temperature. This equation of state was used to calculate other volumetric properties such as isothermal compressibility, isobaric thermal expansibility, differences in isobaric and isochoric heat capacities, thermal pressure coefficient, internal pressure and secant bulk modulus. The results can be used to extend the present equation of state of seawater to higher temperature as a function of pressure.

1 Introduction

The majority of water on earth is seawater. Seawater is a solution of salts of nearly constant composition (Millero et al., 2008), dissolved in variable amounts of water. For scientific investigations and process design of many natural and technical processes, which have to do with seawater, it is of great importance to have a reliable base of thermodynamic data. The most recent standard formulation (IAPWS, 2008) for seawater lacks of density measurements at higher temperature and elevated pressure (IAPWS Certified Research Need #16, 2007), thus this work fills an essential data gap which is in particular important for evaporating tropical estuaries or technical applications such as desalination plants.

In 2006, as a successor of the Joint Panel on Oceanographic Tables and Standards (JPOTS), the Working Group 127 (WG127) has been established by the International Association for the Physical Sciences of the Ocean (IAPSO) and the Scientific Committee on Oceanic Research (SCOR). Its main objective is a recent evaluation of the current standards for seawater thermodynamics and, if necessary, the recommendation of improved formulations. Among the reasons for this revision is the need for consistency between seawater properties and the more accurate recent international standards for temperature (ITS-90) and for properties of pure water (IAPWS-95) (Wagner and Pruß, 2002). As a result, the International Association for the Properties of Water and Steam in cooperation with WG127 endorsed a new joint seawater formulation on its international conference in September 2008 in Berlin (IAPWS, 2008) which is planned to be adopted internationally for oceanography, too (McDougall et al., 2009).

The present equation of seawater for seawater in use as the international standard for oceanography, is the 1980 International Equation of State of Seawater (EOS-80), released by the Joint Panel on Oceanographic Tables and Standards (JPOTS), and published by Millero et al. (1980). It is based on the temperature scale IPTS-68 and on the Practical Salinity Scale 1978, PSS-78 (Lewis and Perkin, 1981). According to the analysis of thermodynamic properties of standard seawater, it has to be pointed out, that, after the evaluation of EOS-80, there were only few new experimental (p, ρ, T) measurements available (Feistel, 2003, 2008) and until 2008 no more recent official standard EOS have been developed for the calculation of the thermodynamic properties of standard seawater.

The purpose of the present study is the construction of a comprehensive and accurate thermodynamic equation of state for seawater over a wider range of salinity, temperature and pressure than the earlier work. This would make it useful to the use of seawater in modeling and industrial processes at high temperatures and pressures.

In this research work, we describe the experimental results for standard seawater, $S=35$, corresponding to an absolute salinity $S_A \approx 35.16504$ g/kg on the new Reference-Composition Salinity Scale (Millero et al., 2008) which extends the current Practical Salinity Scale PSS-78 to temperatures even higher than 40°C. At the first step, the most important literature sources have been analysed.

Tait (1888) was the first scientist, who studied the volumetric properties of seawater.

As a result of this investigations the celebrated Tait equation was developed for describing the density (or specific volume) of liquids at high pressures and temperatures. The range of compressibility results were at temperatures T=(273.15 to 288.15) K and pressures p=(0.1 to 50) MPa.

Ekman (1908) measured the compressions of seawater at T=(273.15 to 293.15) K, p=(0.1 to 60) MPa and at salinities S=(31.13 and 38.53). Higashi et al. (1931) measured the specific gravity and the vapor pressure of concentrated seawater at T=(273.15 to 448.15) K.

Newton and Kennedy (1965) determined the (p,v,T) properties of seawater at T=(273.15 to 298.15) K, p=(0 to 130) MPa and S=(0, 30.52, 34.99 and 41.03). The apparatus consisted of a piston-and-cylinder volumemeter for measuring volume changes, supplemented by a pycnometer to determine the one-atmosphere specific volumes. A sample of standard seawater of salinity S=34.99‰ (so-called Copenhagen seawater) was reported as 35.01‰ on the Point Loma bridge – an apparent accuracy of 2 parts in 10^5. The average uncertainty of specific volume measurements was $\pm 7\times10^{-5}$ cm^3 g^{-1}.

Wilson and Bradley (1966, 1968) measured the specific volumes of seawater at T=(273.15 to 313.54) K, p=(0 to 100) MPa and S=(0 to 40.37). The seawater samples used in this study were supplied by the Navy Oceanographic Office. The samples were natural seawater taken from the Bermuda-Key West Region of the Atlantic Ocean. Biological material was removed prior to the salinity measurements. The uncertainties of these measurements of specific volume were estimated as $\pm 1\times10^{-5}$ cm^3 g^{-1}.

Bradshaw and Schleicher (1970) measured the thermal expansion of seawater at T=(271.15 to 303.15) K, pressures p=(0.8 to 100.1) MPa and salinities S=(30.5, 35 and 39.5). A direct measurements technique was used in which the change of volume of a water sample in a dilatometer was measured with the sample held under constant pressure and subjected to a temperature change. Temperature derivatives of specific volume were derived; it is estimated that the data are accurate to within $\pm 3\times10^{-6}$ cm^3 g^{-1} deg^{-1}.

Duedall and Paulowich (1973) reported isothermal compressibility values of seawater with a precision of $\pm 0.07 \times 10^{-6}\,\mathrm{bar}^{-1}$. The measurements were performed at T=(283.15 and 288.15) K, p=(0 to 90.12) MPa and S=35.

Emmet and Millero(1974) measured the specific volume of S=35 salinity seawater at T=(271.15 to 313.15) K, p=(0 to 99.533) MPa. The specific volume of standard seawater with 19.3755‰ chlorinity has been measured with a high-pressure magnetic float densimeter. The specific volumes were fitted to an equation having a standard deviation of $\pm 11 \times 10^{-6}\,\mathrm{cm}^3\,\mathrm{g}^{-1}$.

The compressibility of distilled water and seawater of S=(30.705, 34.891 and 38.884) salinities were measured by Bradshaw and Schleicher (1976), in 1976, at T=283.15 K, p=(0.8 to 100) MPa using the well known dilatometer method. The Copenhagen Standard Seawater with S=34.912 were used in these experiments. The average uncertainty of this literature data has been estimated as $\Delta v = 15 \times 10^{-6}\,\mathrm{cm}^3\,\mathrm{g}^{-1}$.

The experimental specific volume results of seawater published by Chen and Millero (1976) were presented at T=(273.15 to 313.15) K, pressures p=(0 to 100) MPa and salinities S=(5 to 40). Specific volume of standard seawater sample (P-57, 6/8, 1972, Cl‰=19.3755) has been measured with a high-pressure magnetic float densimeter. The uncertainty of specific volume was $\Delta v = 4 \times 10^{-6}\,\mathrm{cm}^3\,\mathrm{g}^{-1}$.

Caldwell (1978) has measured the temperature-pressure-salinity points of maximum density at T=(267.07 to 276.99) K, pressures p=(0.1 to 38.09) MPa and S=(0 to 29.84).

After the analysis of all available experimental results of (p, v, T) behavior, isothermal compressibility and thermal expansion, Millero et al. (1980) have evaluated the EOS-80.

After the publication and international agreement of EOS-80, the high accurate IAPWS Formulation 1995 for Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use, which has been formulated as the Helmholtz free energy, was developed and published by Wagner and Pruß (2002). A Gibbs function of seawater for the oceanic range of salinities, temperatures and pressure, based on the IAPWS-95 formulation for pure water and the ITS-90 temperature scale, was developed by Feistel (2003) and Feistel and Hagen (1995, 1998), extending the EOS-80 formulation by equations for the entropy, the enthalpy and the chemical potential, and correcting the systematic error of EOS-80 high-pressure sound speeds.

The temperature interval of EOS-80 at $T=(271.15$ to $313.15)$ K is not large enough for various oceanographic or engineering applications. It is strongly necessary to improve the EOS-80 using new density data of pure water (IAPWS-95) (Wagner and Pruß, 2002) and (p, ρ, T) measurements of seawater with various salinities. These should cover a broad range of pressure, temperature and salinity. Among the reasons for this ongoing revision process is the pursuit for consistency between seawater properties and the more accurate recent international standards of temperature (ITS-90).

This information shows the important role of pressure, temperature and salinity in the thermophysical properties of seawater, which are necessary to be investigated over a wide range of state parameters. This investigation of the (p,ρ,T) properties of standard seawater at $T=(273.14$ to $468.06)$ K and $p=(0.101$ to 140 MPa) is the first publication of our group in this field. Work on salinities different from $S=35$ is in preparation.

2 Experimental

The (p, ρ, T) measurements were carried out using a new modernized high pressure – high temperature vibrating tube densimeter DMA HPM (Anton-Paar, Austria). A sketch of the vibration-tube densimeter used in this study is shown in Fig. 1. The measurements with a vibrating tube (13) are based on the dependence of the period of oscillation of a unilaterally fixed U-tube Hastelloy C-276 on its mass. This mass consists of the U-tube material and the mass of the fluid filled into the U-tube. The behavior of the vibrating tube can be described by the simple mathematical-physical mass-spring-damper model (Kratky et al., 1969), where the mass of vibration tube m

is equal to the sum of mass of them in vacuum m_0 and the mass of filled liquid ρV:

$$f(T,p) = \frac{1}{\tau(T,p)} = \frac{1}{2\pi}\sqrt{\frac{k}{m_0 + \rho(T,p)V(T,p)}}, \tag{1}$$

$\tau(T,p)$ in Eq. (1) is the period of oscillation, μs; $f(T,p)$ the corresponding frequency, μs^{-1}; m_0 is the mass of evacuated vibration tube, kg; $V(T,p)$ is the volume of vibration tube, m^3; $\rho(T,p)$ is the density of the filled liquid in the inside of vibration tube, $kg\,m^{-3}$; k is the spring constant of tube material, which depends on the size and shape of the tube and is proportional to the Young's modulus of the tube material, $N{\cdot}m^{-1}$. At given spring constant k the sensitivity increases with increasing ratio of the mass of a fluid to that of the tube, $(\rho V/m_0)$. For glass the sensitivity is large, while for the stainless steel and alloys the sensitivity is lower.

Measurement of the mass of liquid filled into the vibration tube can be performed by measuring its period according to Eq. (1) from which follows:

$$\rho(T,p) = \frac{\frac{\tau^2(T,p)k}{4\pi^2} - m_0}{V(T,p)} = \frac{\tau^2(T,p)k}{4\pi^2 V(T,p)} - \frac{m_0}{V(T,p)}. \tag{2}$$

The period depends on the elasticity and length of the tube. From Eq. (2) it follows, that the frequency of the harmonic oscillation of the vibration tube can be directly related to the density of the fluid:

$$\rho(T,p) = A(T,p) - B(T,p)\tau^2(T,p), \tag{3}$$

where:

$$A(T,p) = -\frac{m_0}{V(T,p)} \quad \text{and} \quad B(T,p) = -\frac{k}{4\pi^2 V(T,p)}.$$

The parameters $A(T,p)$ and $B(T,p)$ were determined by using at least two substances of known density as calibration samples. In this work, water (Wagner and Pruß, 2002) (twice-distilled), methanol (Osada et al., 1999; Yokoyama and Uematsu, 2003; de Reuck and Craven, 1993) and NaCl (aq) (Hilbert, 1979; Archer, 1992) of various molalities were used as reference substances for the calibrating the vibrating tube densitometer.

Unfortunately, the parameters $A(T,p)$ and $B(T,p)$ are temperature and pressure dependent. Therefore, the parameters must be determined for each temperature and pressure separately and the classical equation must be extended by temperature and pressure-dependent terms. For measurements at T=(273.14 to 468.07) K and up to p=140 MPa the following calibration equation containing 14 significant parameters has been employed (Ihmels and Gmehling, 2001):

$$A(T,p) = \sum_i a_i(T/\mathrm{K})^i + \sum_j b_j(p/\mathrm{MPa})^j + c(T/\mathrm{K})(p/\mathrm{MPa}), \tag{4}$$

$$B(T,p) = \sum_i d_i(T/\mathrm{K})^i + \sum_j e_j(p/\mathrm{MPa})^j + f(T/\mathrm{K})(p/\mathrm{MPa}), \tag{5}$$

where: a_0, a_1, a_2, a_3, b_1, b_2, c, d_0, d_1, d_2, d_3, e_1, e_2 and f are the parameters of the these extended vibrating tube equations. The calculated values of A and B shown in Figs. 2 and 3.

The period of vibration tube τ was determined with a digital counter using the vibration tube installation. The counter together with the temperature control unit is implemented inside the DMA HPM control system. This consists of a measuring cell (13) and a modified mPDS2000V3 control unit (9) connected to a PC (15) via an interface (14). The temperature in the measuring cell was controlled using a thermostat (18) F32-ME (Julabo, Germany) with an error of ±10 mK and was measured using the (ITS-90) Pt100 thermometer (AOIP PN 5207) with an experimental error of ±15 mK. Pressure was generated by a pressure intensifier (4) (Type 37-6-30, HIP, USA) and was measured by two different pressure transmitters (HP-1 (5) and P-10 (6), WIKA Alexander Wiegand GmbH & Co., Germany) with an experimental uncertainty of 0.5 and 0.1% from a measured value, respectively. A constant pressure was indicated by a constancy of the counter digits during the experiments. All high pressure valves (2, 7, 8, 16, 17), tubes, fittings (3 and 11) etc. were supplied by SITEC and NOVA (Switzerland).

The mPDS2000V3 control unit displays the vibration period to seven digits. According to the specifications of Anton-Paar and calibration procedures, the observed reproducibility of the density measurements at temperatures T=(273.14 to 468.06) K and at pressures up to p=140 MPa is within $\Delta\rho$=±(0.1 to 0.3) kg m^{-3} or $\Delta\rho$=±(0.01 to 0.03)%.

Before starting experiments, the installation was washed with water, acetone and dried in a vacuum system. The valve of the flask (1) remains closed. Vacuum is applied over (3 to 4) hours using a vacuum pump (19) (Model S 1.5, Leybold, Germany) until a minimal pressure (3 to 5 Pa) has been reached (measured with digital vacuum indicator 10) THERMOVAC TM 100 (Leybold, Germany). The valve (17) is closed and the valve of the flask is opened. The investigated substance is filled into the measuring system. A special window (12) was constructed to tracing of the flow of measured samples between valves (16) and (17). After filling the system, the valves (2) and (16) were closed. The high pressure region is restricted to the space between these two valves (bold lines in Fig. 1). The experiments were started usually at low pressure (0.8 to 1.0 MPa). The time needed for the temperature stabilization was about (50 to 60) min. The period of oscillation of the vibration tube is taken from the display of the mPDS2000V3 control system (9).

3 Results and discussion

The (p, ρ, T) data of the standard seawater samples (S=34.993, k_{15}=0.99982, 10 October 2006 and S=34.994, k_{15}=]0.99984, 5 October 2007, OSIL Lab., UK) were measured at T=(273.14 to 468.06) K, pressures up to p=140 MPa and a new equation of state for the standard seawater is reported. The temperature and pressure steps in the experiments were approximately T=(5 to 20) K and p=(5 to 10) MPa, respectively.

Obtained values were compared with the available literature results of standard seawater at T=(273.15 to 313.15) K and pressures up to p=130 MPa and good agreements were received. The obtained (p, ρ, T) results are listed in Appendices.

The measured densities as a function of pressure and temperature were fitted to the Equation of state (1) from Safarov (2003):

$$p/\text{MPa} = A(\rho/\text{g}\,\text{cm}^{-3})^2 + B(\rho/\text{g}\,\text{cm}^{-3})^8 + C(\rho/\text{g}\,\text{cm}^{-3})^{12}, \tag{6}$$

where: the coefficients of Eq. (6) $A(T)$, $B(T)$ and $C(T)$ are functions of temperature.

$$A(T) = \sum_{i=1}^{4} a_i T^i, \quad B(T) = \sum_{i=0}^{3} b_i T^i, \quad C(T) = \sum_{i=0}^{3} c_i T^i. \tag{7}$$

The coefficients a_i, b_i and c_i for Eqs. (6) and (7) are given in Table 1. The Eqs. (6–7) describe the experimental results of density of standard seawater within ±0.006%, corresponding to 0.084 kg m^{-3} standard with a maximal deviation of 0.280 kg m^{-3}.

Figures 4–6 show plots of pressure p of standard seawater vs. density ρ, of density ρ of standard seawater vs. temperature T at pressures calculated by Eqs. (6–7) and deviations of experimental density ρ_{exp} of standard seawater from the calculated density ρ_{cal} by Eqs. (6–7) vs. pressure p.

The isothermal compressibility k_T/MPa^{-1} of the standard seawater is a measure for the relative volume change of a fluid as a response to a pressure change at constant temperature:

$$k_T = (1/\rho)(\partial p/\partial \rho)_T^{-1}. \tag{8}$$

The pressure in the oceans changes with by about one atmosphere per 10 m. So the pressure at 100 m depth is about 1 MPa, at 1000 m it is about 10 MPa. The pressure range found in seawater goes from approximately 0.1 MPa at sea surface level to about 108.6 MPa at the deepest known place, the Mariana Trench (11 022 m), this is 1000 times higher than the standard atmospheric pressure at sea level. The isothermal compressibility of seawater can be calculated from the experimental (p, ρ, T) results of the standard seawater using Eqs. (6–7) according to :

$$k_T = 1/[2A(T)\rho^2 + 8B(T)\rho^8 + 12C(T)\rho^{12}]. \tag{9}$$

The calculated values of the isothermal compressibility are given in Appendices and are shown in Fig. 7 vs. pressure p and in Fig. 8 vs. temperature T.

The other thermal property, which can be calculated from Eqs. (6–7) is isobaric thermal expansibility α_p/K^{-1}, which is the tendency of matter to change in volume in response to a change in temperature at constant pressure. Samples that contract with an increase in temperature are very uncommon; this effect is limited in size, and only occurs at low salinity and temperature, below the temperature of maximum density (Caldwell, 1978). The degree of expansion divided by the change in temperature is called the sample's coefficient of isobaric thermal expansibility and generally varies with temperature.

$$\alpha_p = (1/\rho)(\partial p/\partial T)_\rho(\partial p/\partial \rho)_T^{-1}. \tag{10}$$

The known temperature range, which occurs in natural seawater, ranges from the freezing point to approximately maximum T=(303.15 to 313.15) K. At active ridge systems (2000 to 3000 m) the temperatures can be extremely hot as seawater gushes out of fissures in the underlying rocks (473.120 to 673.15) (Sun, 2008). These temperatures decrease quickly as these hot waters mix with the surrounding cold water (276.15 to 277.15 K). The isobaric thermal expansibility of seawater is important to be known for these hot processes and is necessary to be calculated from the constructed equation of state. It can be calculated from the experimental (p, ρ, T) results of the standard seawater using Eqs. (6–7):

$$\alpha_p = [A'(T) + B'(T)\rho^6 + C'(T)\rho^{10}]/[2A(T) + 8B(T)\rho^6 + 12C(T)\rho^{10}], \tag{11}$$

where: $A,$ B, and C are the derivatives of the $A,$ B,and C:

$$A'(T) = \sum_{i=1}^{3} i a_i T^{i-1}, \quad B'(T) = \sum_{i=1}^{2} i b_i T^{i-1}, \quad C'(T) = \sum_{i=1}^{2} i c_i T^{i-1}. \tag{12}$$

The calculated values of the isobaric thermal expansibility are given in Appendices and shown in Fig. 9.

The next important thermodynamic property of interest is the difference of specific heat capacities $(c_p - c_v)/\mathrm{J\,kg^{-1}\,K^{-1}}$. Measuring the heat capacity at constant volume can be prohibitively difficult for liquids. Instead it is easier to measure the heat capacity at constant pressure and solving for the heat capacity at constant volume using mathematical relationships derived from basic thermodynamic laws:

$$c_p = c_v + T\frac{(\partial p/\partial T)_\rho^2}{\rho^2(\partial p/\partial \rho)_T}, \tag{13}$$

where: c_p and c_v are the heat capacities at constant pressure and volume, respectively. Using Eqs. (9) and (11), we can find the following relationship:

$$c_p - c_v = \frac{\alpha_T^2 T}{\rho k_T}. \tag{14}$$

The calculated values of the differences in specific heat capacities of the standard seawater are given in Appendices and are shown in Fig. 10.

The thermal pressure coefficient $\gamma/\mathrm{MPa\,K^{-1}}$ is calculated as the ratio of the isobaric thermal expansibility to the isothermal compressibility at the same state parameters S, T and p:

$$\gamma = \frac{\alpha_p}{k_T}. \tag{15}$$

The calculated values of thermal pressure coefficient of the standard seawater are given in Table 1 and shown in Fig. 1.

The internal pressure, $p_{\mathrm{int}}/\mathrm{MPa}$ is related to thermal pressure coefficient, γ, and defined by the following relationship:

$$p_{\mathrm{int}} \equiv \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = T\gamma - p = \frac{T\alpha_p}{k_T} - p. \tag{16}$$

The calculated values of internal pressure of the standard seawater are given in Appendices and shown in Fig. 12.

The next important thermodynamic property of the analysis of quality of measured values is secant bulk modulus of standard seawater. Most substances diminish in volume when exposed to a uniform, externally applied pressure. Secant bulk modulus K/MPa is the product of the original fluid volume and the slope of the line drawn from the origin to any specified point on the plot of pressure versus specific volume (the slope of the secant line to the point).

$$K = \frac{v^o p}{v^o - v^p}, \tag{17}$$

where: K/MPa is the secant bulk modulus, v^0 is the specific volume at the reference temperature and pressures, v^p is the experimental values of specific volume at the reference temperature and pressures, p is the experimental pressure.

Because the specific volumes ratio is dimensionless, units of bulk modulus are the same as pressure, MPa. Thus, the bulk modulus is a measure of resistance against the compressibility of a fluid. The calculated values of secant bulk modulus, K/MPa of the standard seawater are given in Appendices and their dependence on pressure p is shown in Fig. 13. From this dependence, it is to be seen, that the secant bulk modulus for standard seawater is approximately a linear function of pressure.

Measured (p, ρ, T) results of standard seawater were compared with the available literature results (Feistel, 2003; Newton and Kennedy, 1965; Wilson and Bradley, 1968; Emmet and Millero, 1974; Chen and Millero, 1976; Feistel and Hagen, 1995, 1998) and are shown in Fig. 14. The 84 experimental (p, ρ, T) results of standard seawater at S=34.99, measured by Newton and Kennedy (1965), showed $\Delta\rho$=±0.017% average deviation with our experimental values. The maximum uncertainty of results (Newton and Kennedy, 1965) is $\Delta\rho$=0.037% at T=273.15 K and p=0.101 MPa. The (p, ρ, T) results of Newton and Kennedy (1965) are usually smaller than our results up to p=40 MPa and at higher pressures they are higher than owns.

The 134 experimental (p, ρ, T) results of seawater at S=35.568, measured by Wilson and Bradley (1968), also were compared with our results at S=34.993. The salinity of seawater sample used in Wilson and Bradley (1968) higher than salinity of seawater sample used in our experiments. In this case, the average deviation of (Wilson and Bradley, 1968) from our results is higher $\Delta\rho$=0.046%. The maximum uncertainty of (Wilson and Bradley, 1968) is $\Delta\rho$=0.068% at T=274.38 K and p=0.101 MPa.

The 152 experimental (p, ρ, T) results of seawater Emmet and Millero (1974) at S=35 have $\Delta\rho$=±0.009% average deviation from our results and are smaller than our results up to appr. p=40 MPa. The maximum uncertainty of density results of Emmet and Millero (1974) is $\Delta\rho$=0.048% at T=273.15 K, p=0 MPa.

The 97 (p, ρ, T) results of seawater Chen and Millero (1976) at S=35.003 have also been compared with our results. The average deviation of Chen and Millero (1976) from our measurements is $\Delta\rho$=±0.008%. The (p, ρ, T) results of Chen and Millero (1976) are smaller than our results up to p=50 MPa. The maximum uncertainty of (p, ρ, T) results in Chen and Millero (1976) is $\Delta\rho$=0.040% at T=273.15 K, p=0 MPa.

The 144 experimental density values of seawater at T=(273.14 to 313.21) K and pressures up to p=140 MPa have also been compared with calculated results of Feistel, 2003; Feistel and Hagen, 1995, 1998. The average deviation of these results with our measurements was $\Delta\rho$=±0.007%. The maximum uncertainty of (p, ρ, T) results in Feistel, 2003; Feistel and Hagen, 1995, 1998, is $\Delta\rho$=0.020% at T=283.13 K and p=20.031 MPa.

The calculated isothermal compressibility and isobaric thermal expansibility results of standard seawater published in Chen and Millero (1976). We compared our calculated results of isothermal compressibility (99 points) and isobaric thermal expansibility (99 points) with the results of Chen and Millero (1976). The average deviation of isothermal compressibility results with our calculated results is $\Delta k_T=\pm 2.7\times 10^{-6}$ MPa^{-1}. The maximum uncertainty is $\Delta k_T=-10.1\times 10^{-6}$ MPa^{-1} at T=288.14 K and p=10 MPa. The average deviation of isobaric thermal expansibility α_p/K^{-1} results in Chen and Millero (1976) and our calculated results is $\Delta\alpha_p=\pm 9.8\times 10^{-6}\,\mathrm{K}^{-1}$. The maximum uncertainty was $\Delta\alpha_p=41.56\times 10^{-6}\,\mathrm{K}^{-1}$ at $T=273.14$ K and $p=0$ MPa.

Calculated values of secant bulk modulus were compared with the published literature results from Millero et al. (1980). Differences of both calculated values: at $T=273.15$ K, $p=100$ MPa was $\Delta K=\pm 24$ MPa and at $T=298.15$ K, $p=100$ MPa was $\Delta K=\pm 22$ MPa.

4 Conclusions

This study presents new (p, ρ, T) measurements of standard seawater samples in the interval of state parameters (at $T=(273.14$ to $468.06)$ K and pressures up to $p=140$ MPa) were measured. The results can be used to extend the equation of state of seawater to higher temperature and pressures. The new equation of state can be used to calculate a number of thermal and caloric parameters.

During the analysis of the isothermal compressibility values of standard seawater it became obvious that standard seawater has similar anomalies as pure water (Appendices and Figs. 4, 5, 7–12). The main part of standard seawater (appr. 96.5%) is pure water. In a typical liquid the compressibility decreases as the structure becomes more compact due to lower temperature. In water and all aqueous salt solutions, in which the concentration of water is very high, the cluster equilibrium is shifted towards the more open structure (for example, expanded structure – ES) as the temperature is reduced due to favoring the more ordered structure (that is, ΔG for ES document CS (collapsed structure) becomes more positive). As the water structure is more open at these lower temperatures, the capacity for it to be compressed increases (Kell, 1975). The effect is not a simple dependency on density, however, or else the minimum at $T=319.65$ K for isothermal (that is, without change in temperature) compressibility of pure water. For the compressibility depends on fluctuations in the specific volume, these will be large where water molecules fluctuate between being associated with a more open structure, or not, and between the different environments within the water clusters. At high pressures (for example, ∼200 MPa) this compressibility anomaly, although still present, is far less apparent (Kanno and Angell, 1979).

The isobaric thermal expansibility of seawater is increasing with the increasing of pressure up to about T=313.15 K (in which the isobaric thermal expansibility appr. is constant) in contrast to most other liquids where thermal expansibility decreases with increased pressure. Above T=313.15 K, isobaric thermal expansibility of seawater decreases with increased pressure. This is due to the collapsed structure of water having a greater isobaric thermal expansibility than the expanded structure and the increasing pressure shifting the equilibrium towards a more collapsed structure.

These results were used for the development of a new equation of state for seawater. Obtained results can also be used for oceanographic calculations and marine research.

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Table 1. Values of the coefficients a_i, b_i and c_i in Eqs. (6–7).

a_i	b_i	c_i
a_1=-2.157761589	b_0=3638.11368199	c_0=-2235.76774015
a_2= -0.10341365·10^{-2}	b_1= -27.97107636	c_1= 17.6361364636
a_3= 0.103809737·10^{-4}	b_2= 0.0815083395	c_2= -0.04771579895
a_4= -0.305662763·10^{-8}	b_3= -0.74604739·10^{-4}	c_3= 0.4100691661·10^{-4}

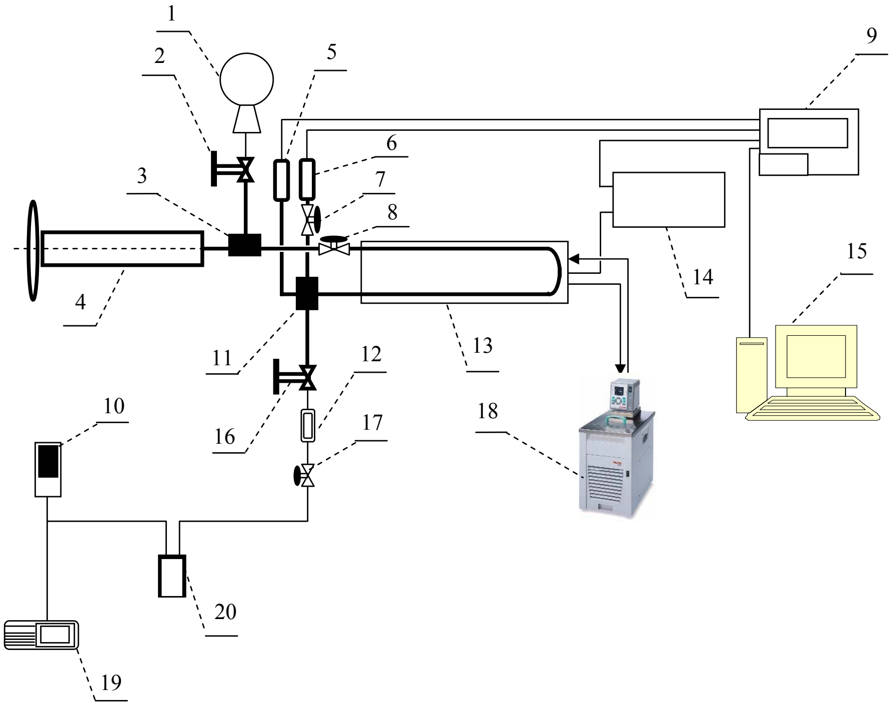

Fig. 1. A new modernized high pressure – high temperature vibrating tube densimeter DMA HPM: 1 – flask for the probe; 2, 7, 16, 17 – valves; 3, 11 – fitting; 4 – pressure intensifier; 5 – pressure sensor HP-1; 6 – pressure sensor P-10; 8 – valve for the closing of system during the experiments; 9 – display mPDS2000V3 for the temperature and frequency control; 10 – vacuum indicator; 12 – visual window; 13 – vibration tube; 14 – interface mode; 15 – PC; 18 – thermostat F32-ME; 19 – vacuum pump; 20 – thermos for cooling.

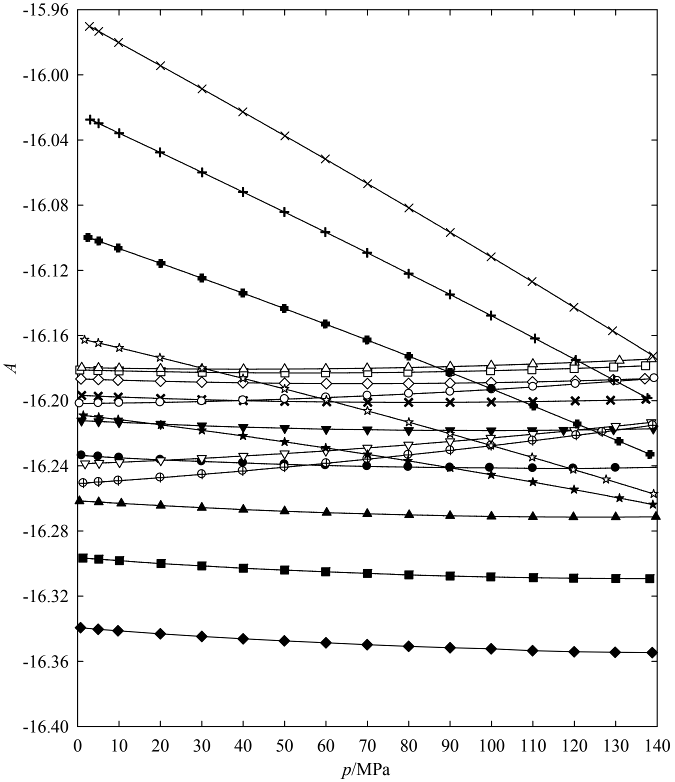

Fig. 2. Plot of calibration coefficient *A* of Eq. (4) of standard seawater vs. pressure *p*: ◆, 273.17 K; ■, 278.15 K; ▲, 283.15 K; ●, 288.16 K; ▼, 293.15 K; ✖, 298.18 K; ◊, 303.18 K; □, 308.15 K; △, 313.15 K; ❍, 333.15 K; ▽, 353.16 K; ⊕, 373.15 K; ★, 393.17 K; ☆, 413.15 K; ✚, 433.18 K; +, 453.17 K; x, 468.03 K.

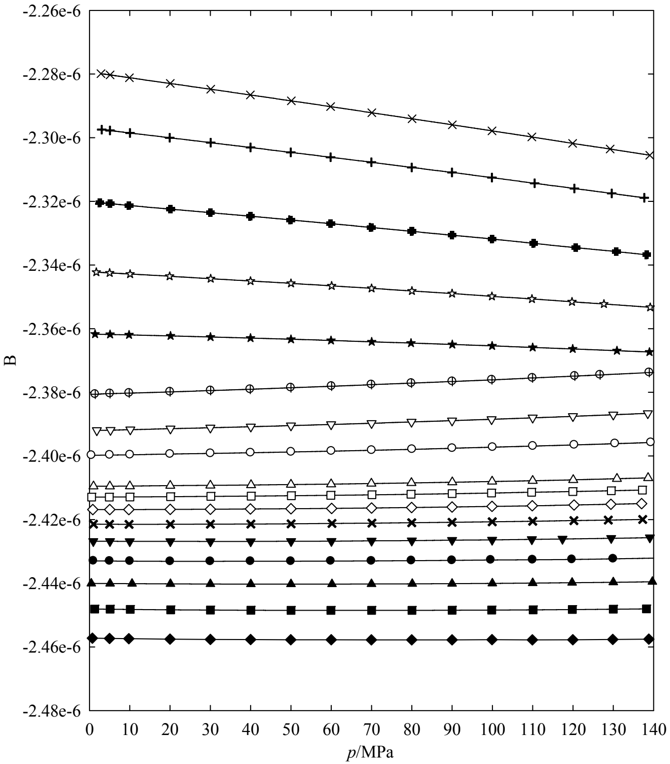

Fig. 3. Plot of calibration coefficient *B* of Eq. (5) of standard seawater vs. pressure *p*: ◆, 273.17 K; ■, 278.15 K; ▲, 283.15 K; ●, 288.16 K; ▼, 293.15 K; ✖, 298.18 K; ◊, 303.18 K; □, 308.15 K; △, 313.15 K; ❍, 333.15 K; ▿, 353.16 K; ⊕, 373.15 K; ★, 393.17 K; ☆, 413.15 K; ✚, 433.18 K; +, 453.17 K; x, 468.03 K.

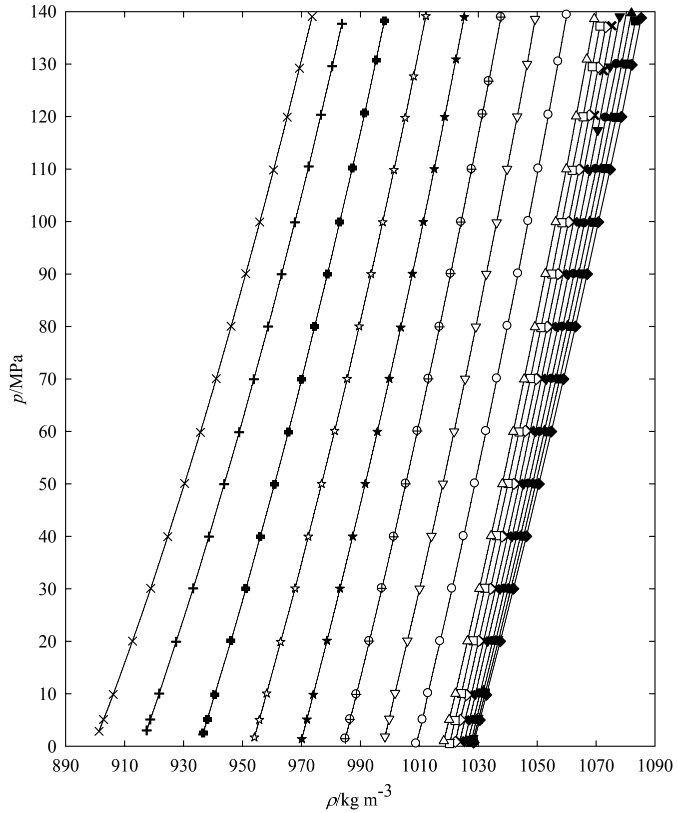

Fig. 4. Plot of pressure p of standard seawater vs. density ρ: ◆, 273.17 K; ■, 278.15 K; ▲, 283.15 K; ●, 288.16 K; ▼, 293.15 K; ✖, 298.18 K; ◊, 303.18 K; □, 308.15 K; △, 313.15 K; ❍, 333.15 K; ▽, 353.16 K; ⊕, 373.15 K; ★, 393.17 K; ☆, 413.15 K; ✚, 433.18 K; +, 453.17 K; x, 468.03 K_calculated by Eqs. (6–7).

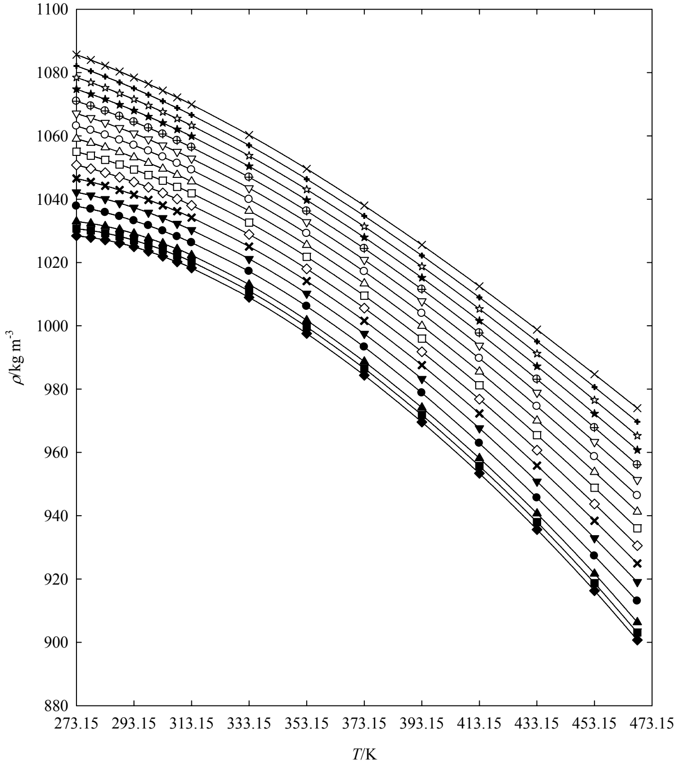

Fig. 5. Plot of density ρ of standard seawater vs. temperature T calculated by Eqs. (6–7): ◆, 0.101 MPa (after T=373.15 K–p_s of water); ■, 5 MPa; ▲, 10 MPa; ●, 20 MPa; ▼, 30 MPa; ✖, 40 MPa; ◊, 50 MPa; □, 60 MPa; ▵, 70 MPa; ❍, 80 MPa; ▿, 90 MPa; ⊕, 100 MPa; ★, 110 MPa; ☆, 120 MPa; ✚, 130 MPa; x, 140 MPa.

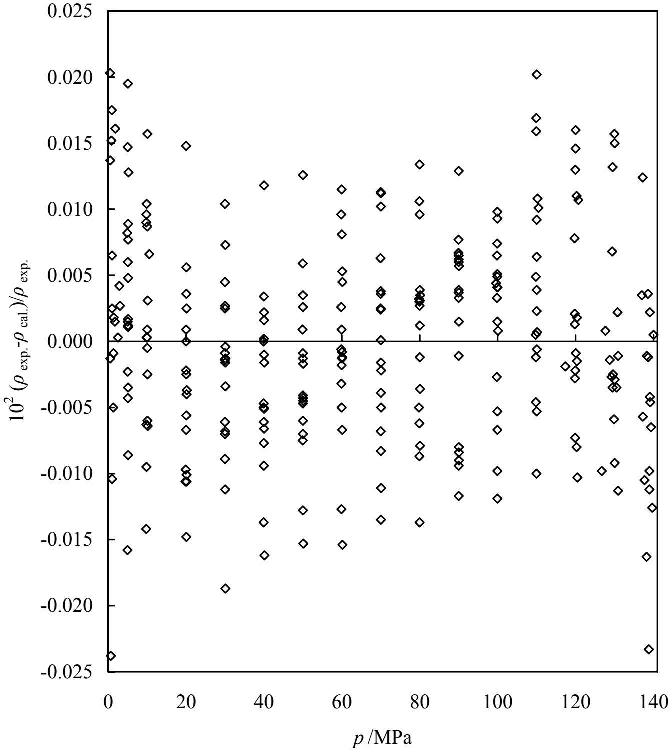

Fig. 6. Plot of deviations of experimental density ρ_{exp} of the investigated standard seawater from the calculated by Eqs. (6–7) density ρ_{cal} vs. pressure p at $T=(273.14 \text{ to } 468.06)$ K.

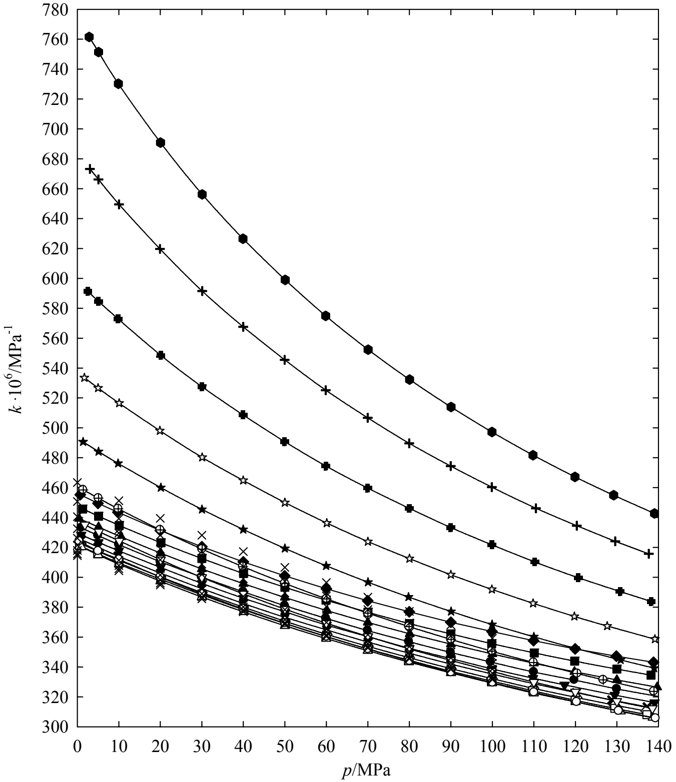

Fig. 7. Plot of isothermal compressibility $k_T \times 10^6$/MPa^{-1} of standard seawater vs. pressure p: ◆, 273.17 K; ■, 278.15 K; ▲, 283.15 K; ●, 288.16 K; ▼, 293.15 K; ✕, 298.18 K; ◊, 303.18 K; □, 308.15 K; △, 313.15 K; ❍, 333.15 K; ▽, 353.16 K; ⊕, 373.15 K; ★, 393.17 K; ☆, 413.15 K; ✚, 433.18 K; +, 453.17 K; ⬢, 468.03 K; x (Millero et al., 1980).

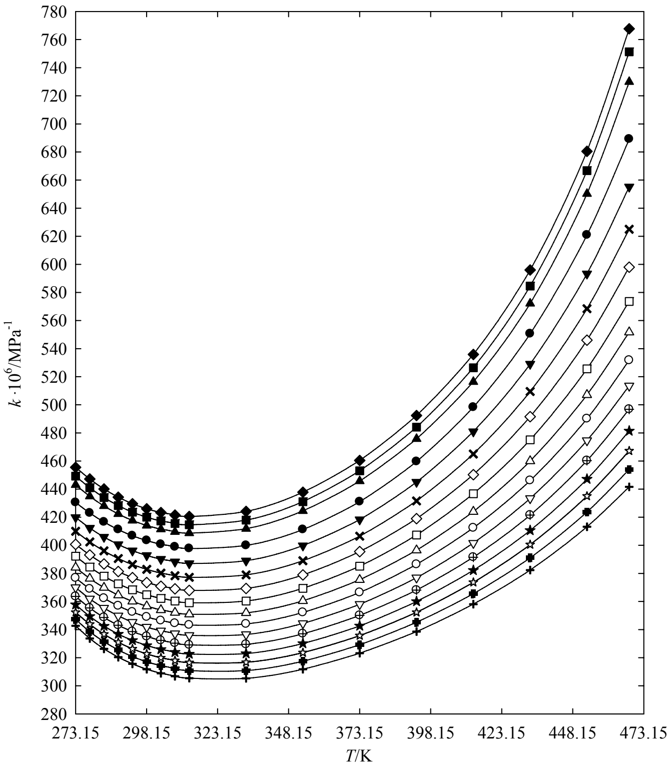

Fig. 8. Plot of isothermal compressibility $k_T \times 10^6$/MPa^{-1} of standard seawater vs. temperature T: ◆, 0.101 MPa (after T=373.15 K–p_s of water); ■, 5 MPa; ▲, 10 MPa; ●, 20 MPa; ▼, 30 MPa; ✖, 40 MPa; ◊, 50 MPa; □, 60 MPa; △, 70 MPa; ❍, 80 MPa; ▽, 90 MPa; ⊕, 100 MPa; ★, 110 MPa; ☆, 120 MPa; ✚, 130 MPa; +, 140 MPa.

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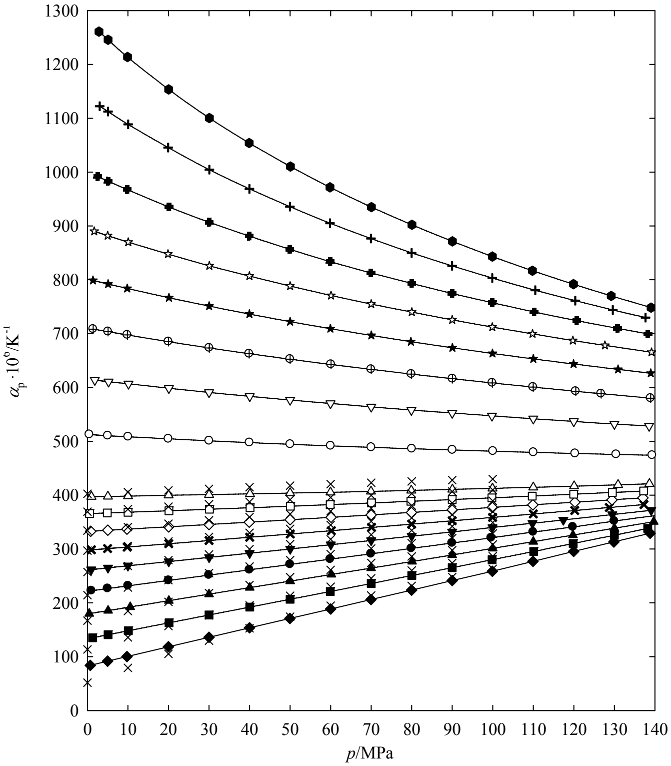

Fig. 9. Plot of isobaric thermal expansibility $\alpha_p \times 10^6$/K^{-1} of standard seawater vs. pressure p: ◆, 273.17 K; ■, 278.15 K; ▲, 283.15 K; ●, 288.16 K; ▼, 293.15 K; ✖, 298.18 K; ◊, 303.18 K; □, 308.15 K; ▵, 313.15 K; ❍, 333.15 K; ▿, 353.16 K; ⊕, 373.15 K; ★, 393.17 K; ☆, 413.15 K; ✚, 433.18 K; +, 453.17 K; ⬢, 468.03 K; x (Millero et al., 1980).

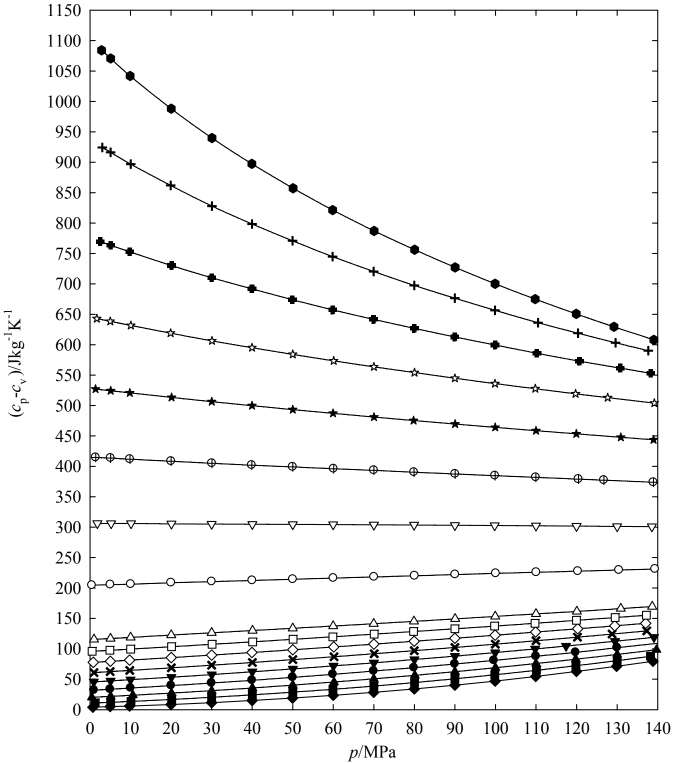

Fig. 10. Plot of difference in isobaric and isochoric heat capacities (c_p-c_v)/Jkg^{-1} K^{-1} of standard seawater vs. pressure p: ◆, 273.17 K; ■, 278.15 K; ▲, 283.15 K; ●, 288.16 K; ▼, 293.15 K; ✖, 298.18 K; ◊, 303.18 K; □, 308.15 K; △, 313.15 K; ○, 333.15 K; ▽, 353.16 K; ⊕, 373.15 K; ★, 393.17 K; ☆, 413.15 K; ✚, 433.18 K; +, 453.17 K; ⬢, 468.03 K.

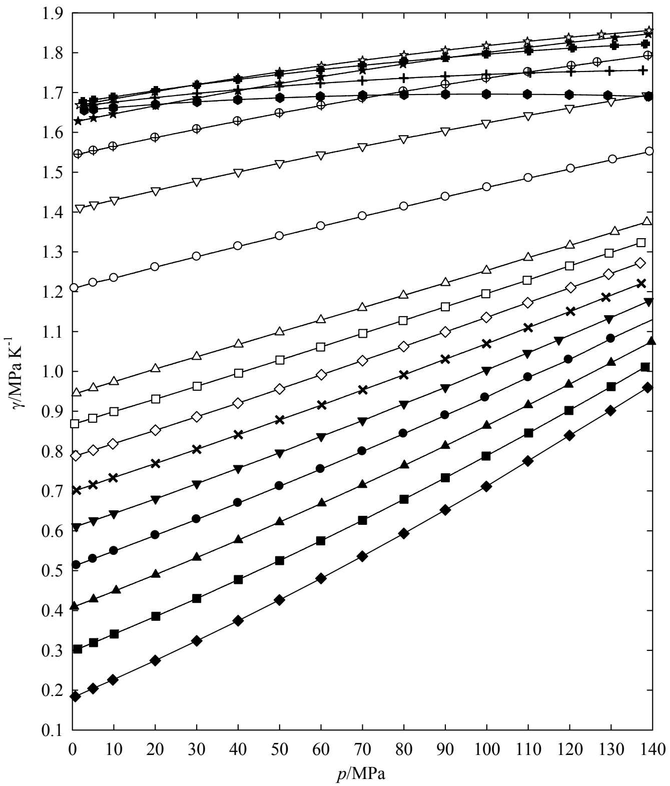

Fig. 11. Plot of thermal coefficient of pressure γ/MPa K^{-1} of standard seawater vs. pressure p: ◆, 273.17 K; ■, 278.15 K; ▲, 283.15 K; ●, 288.16 K; ▼, 293.15 K; ✕, 298.18 K; ◊, 303.18 K; □, 308.15 K; △, 313.15 K; ○, 333.15 K; ▽, 353.16 K; ⊕, 373.15 K; ★, 393.17 K; ☆, 413.15 K; ✚, 433.18 K; +, 453.17 K; ⬢, 468.03 K.

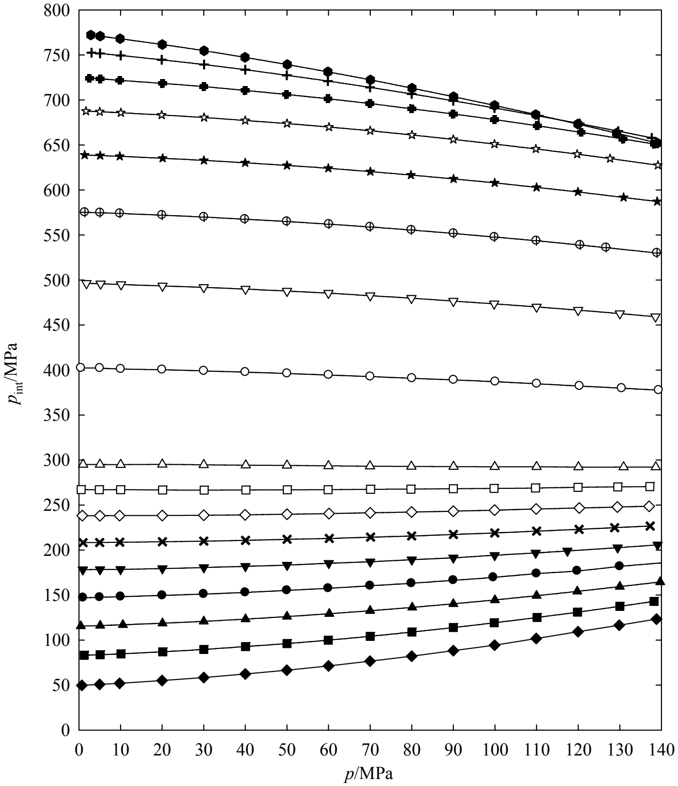

Fig. 12. Plot of internal pressure p_{int}/MPa of standard seawater vs. pressure p: ◆, 273.17 K; ■, 278.15 K; ▲, 283.15 K; ●, 288.16 K; ▼, 293.15 K; ✕, 298.18 K; ◊, 303.18 K; □, 308.15 K; △, 313.15 K; ❍, 333.15 K; ▽, 353.16 K; ⊕, 373.15 K; ★, 393.17 K; ☆, 413.15 K; ✚, 433.18 K; +, 453.17 K; ⬢, 468.03 K.

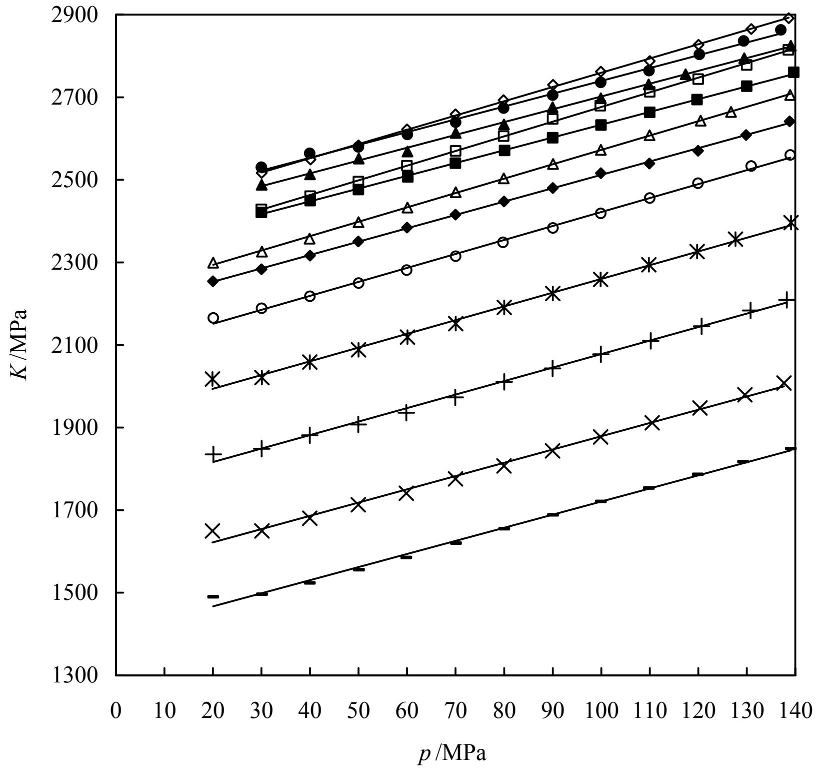

Fig. 13. Plot of calculated values of secant bulk modulus K/MPa of standard seawater vs. pressure p: ◆, 273.17 K; ■, 283.15 K; ▲, 293.15 K; ●, 303.18 K; ◊, 313.15 K; □, 353.16 K; △, 373.15 K; ❍, 393.17 K; *, 413.15 K; +, 433.18 K; x, 453.17 K; –, 468.03 K.

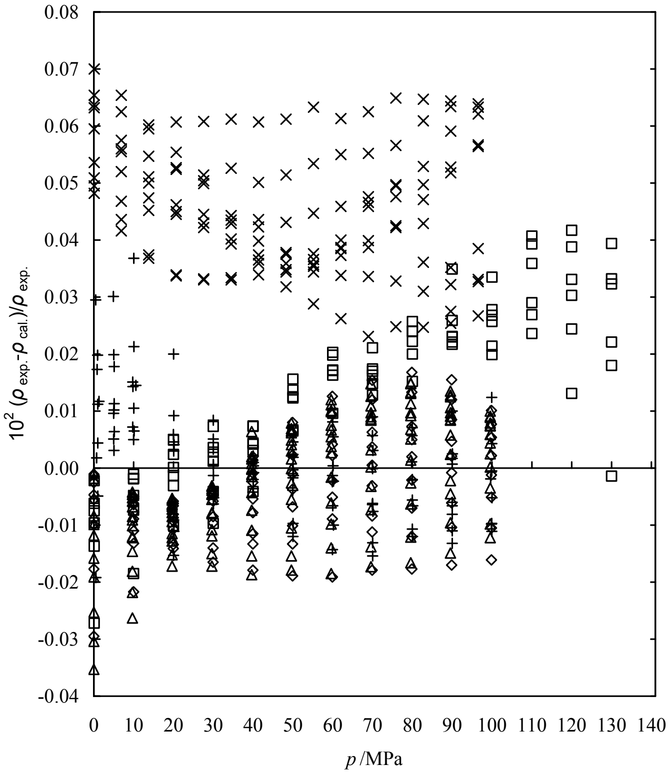

Fig. 14. Comparison of (p, ρ, T) results of standard seawater with various literature values: +, (Feistel, 2003; Feistel and Hagen, 1995, 1998); □, (Newton and Kennedy, 1965); x, (Wilson and Bradley, 1965); △, (Emmet and Millero, 1974); ◇, (Millero et al., 1980).