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Thermophysical properties of seawater: A review and new correlations that include pressure dependence

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Abstract

In a previous paper, the authors have given correlations for seawater thermophysical properties as functions of temperature and salinity, but only for near atmospheric pressures. Seawater reverse osmosis (SWRO) systems operate routinely at pressures of 6 MPa or more; however, experimental data for seawater properties at elevated pressures (P = 0.1-12 MPa) are limited to a salinity of 56 g/kg. To accurately model and design SWRO and thermal desalination systems, a reliable method of estimating the effect of pressure on seawater properties is required. In this work, we present this method and new correlations for seawater thermophysical properties that are valid within the range: t = 0-120 °C, S = 0-120 g/kg, and P = 0-12 MPa. Seawater isothermal compressibility data, available until a salinity of 56 g/kg, were used to develop a correlation for compressibility that is extrapolated to 160 g/kg. Thermodynamic identities were then used to develop accurate pressure dependent correlations for seawater: density, isobaric expansivity, specific heat capacity, enthalpy, entropy and Gibbs energy. New correlations were proposed for seawater: vapor pressure, thermal conductivity and activity of water. Recent work on seawater

surface tension and osmotic coefficient were reviewed. Uncertainty bounds were calculated for each correlation.

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Nomenclature

a	activity	
Cl	chlorinity	g kg^{-1}
c_P	specific heat at constant pressure	J kg^{-1} K^{-1}
g	specific Gibbs energy	J kg^{-1}
h	specific enthalpy	J kg^{-1}
k	thermal conductivity	W m^{-1} K^{-1}
m	molality	moles kg^{-1}
P	pressure	MPa
p_v	vapor pressure	Pa
R	universal gas constant	J mol^{-1} K^{-1}
s	specific entropy	J kg^{-1} K^{-1}
S	salinity	g kg^{-1}
S_K	Knudsen salinity	g kg^{-1}
S_P	practical salinity	g kg^{-1}
S_R	reference-composition salinity	g kg^{-1}
T	absolute temperature	K
t	Celsius temperature	^{o}C
T_0	environmental dead state temperature	K
x	mass fraction	

Greek

Symbols

β_P	isobaric thermal expansivity	K^{-1}
γ	surface tension	mN m^{-1}
κ_T	isothermal compressibility	MPa^{-1}
π	osmotic pressure	MPa
ρ	density	kg m^{-3}
φ	osmotic coefficient	

Subscripts

s	sea salt
sw	seawater
w	pure water

1. Introduction

Millions of people around the world rely on seawater desalination for their drinking water needs [1]. With increasing populations and limited freshwater resources, the demand for desalination is steadily increasing. For designing and optimizing desalination systems, engineers require accurate, simple, and easy-to-use seawater property correlations. Some of the authors of this paper, led by Sharqawy in 2010, have previously developed simple polynomial correlations for calculating the thermophysical properties of seawater in engineering applications [2]. However, the correlations presented by Sharqawy et al. were functions of only temperature and salinity, with the effect of pressure on the properties largely neglected. Accurate thermodynamic equations of state for scientific [3] and industrial [4] use, including pressure dependence, have been made by the International Association for the Properties of Water and Steam (IAPWS). However, there are crucial gaps that are yet to be filled. Experimental data on seawater properties data at pressures beyond atmospheric pressures is limited, particularly for subcooled seawater. For subcooled seawater and for pressures greater than 1 MPa, experimental data is only available for volumetric properties of such as seawater density, speed of sound and expansivity. Furthermore, the available experimental volumetric data is limited to a salinity of 56 g/kg [5].

Pressure dependent properties are important for the desalination industry. Various desalination technologies operate at elevated pressures: UF operates in the range of 0 to 0.5 MPa [6], NF from 0.035 to 4.0 MPa [7–9], brackish reverse osmosis operates in the range of 1.0 to 4.0 MPa [7], and seawater reverse osmosis (SWRO) in the range of 5.5 to 8.5 MPa [7]. Osmotically driven processes such as Pressure Retarded Osmosis (PRO) and the more recently introduced Assisted Forward Osmosis (AFO) may experience pressures above 4.7 MPa [10,11] and 0.6 MPa

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respectively [12]. Unconventional reverse osmosis configurations have also recently been investigated for treating oil and gas produced water to salinities near saturation values of 260 g/kg and pressures near 30 MPa [13]. For accurately modeling conventional and unconventional desalination technologies, there is a need for accurate prediction of the thermophysical properties of seawater at elevated pressures and salinities. In this paper, several results are obtained. The pressure dependence of seawater properties was predicted using thermodynamic principles and inferences from the variation of aqueous sodium chloride thermophysical properties with pressure. The correlations previously proposed by Sharqawy et al. [2] have been updated to include pressure dependence. New correlations have also been proposed for improved accuracy, and a review of recent work on seawater properties is also presented.

Seawater is a mixture of dissolved salts in pure water. A remarkable characteristic of seawater is that the relative chemical composition of seawater is fairly uniform around the world. This allows seawater to be treated as an aqueous solution of a single salt at varying concentration by using "Absolute Salinity," defined to be the "mass fraction of dissolved materials in seawater" [14]. The physical properties of seawater can thus be expressed as function of just temperature, pressure, and salinity. The mass fraction of dissolved salt in seawater, however, is difficult to measure directly. Thus, several salinity scales have been historically used to approximate it: "Knudsen Salinity" (S_K) [15], "Chlorinity" (Cl) [16], "Practical Salinity" (S_P) [17], and, most recently, "Reference Salinity" (S_R) [14]. Correlations given in this paper are expressed as functions of Reference Salinity with the brief term "salinity" (S) used in the paper to mean "Reference Salinity". Temperature scales have also undergone revisions over the past 100 years, such as the International Practical Temperature Scale of 1968 (IPTS-68) and the current

standard, the International Temperature Scale of 1990 (ITS-90). These scales have been described by Preston-Thomas [18] with analytical equations for inter-conversion proposed by Goldberg and Weir [19] and Rusby [20]. Correlations given in this paper are all expressed as functions of the ITS-90 temperature scale. Whenever older datasets in the literature were used to verify newly formulated correlations, such as for the specific heat capacity of seawater, equations from Rusby [20] were used to convert from IPTS-68 to ITS-90.

Several correlations and equations of state for the thermophysical properties of seawater have been proposed over the years. These include: the International Equation of State of 1980 (EOS-80) [21], the IAPWS-08 equation of state for seawater [3], correlations for engineering applications developed by Sharqawy et al. [2], and the recent IAPWS industrial formulation of seawater (IAPWS-14) [4].

EOS-80 [21,22] allowed for accurately calculating the volumetric properties of seawater for the range of temperatures, salinities and pressures: $4 \leq t \leq 40$ °C, $0 \leq S \leq 42$ g/kg and $0 \leq P \leq 100$ MPa. In 2003, Feistel [23] developed a single Gibbs function to express a complete equation of state for seawater. All other thermodynamic properties, such as density, enthalpy and entropy, were derived from the Gibbs function. The Gibbs function of seawater was expressed as a summation of the Gibbs energy of pure water obtained from the IAPWS-95 formulation for pure water and a separate Gibbs function for the saline part of seawater. This formulation underwent revisions [24] and was accepted as the IAPWS-08 formulation for the equation of state for seawater. The IAPWS-08 equation of state was accurate with the saline part being a 64-term polynomial.

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While the IAPWS-08 formulation was accurate and internally consistent, its validity at elevated pressures is limited to certain regions within the temperature, salinity and pressure range: $-10 \leq t \leq 80$ °C, $0 \leq S \leq 120$ g/kg and $0 \leq P \leq 100$ MPa. For near atmospheric pressures, IAPWS-08 was valid for: $-2 \leq t \leq 80$ °C and $0 \leq S \leq 120$ g/kg. Here, near atmospheric pressures refers to atmospheric pressure for temperatures less than the boiling point of seawater ($t \leq 100$ °C) while the pressure was the vapor pressure of seawater for temperatures greater than the seawater boiling point. For elevated pressures for subcooled seawater, the formulation was limited to oceanographic temperatures, salinities and pressures: $-2 \leq t \leq 40$ °C, $0 \leq S \leq 42$ g/kg and $0 \leq P \leq 100$ MPa. While the IAPWS-08 equation was adopted for use in oceanography and scientific studies, its computational intensity and range limitation up to a temperature of 80 °C made it less appropriate for use in the desalination industry. Furthermore, IAPWS-08 did not address transport properties such as thermal conductivity, viscosity and multiphase properties such as surface tension. Thus, in 2010, Sharqawy et al. [2], compiled a detailed review of seawater properties including properties not discussed in IAPWS-08 and, developed simple polynomial correlations for engineering applications. Past experimental data from the literature were converted to the latest ITS-90 temperature and "reference salinity" scales and used in the correlations. Problems in EOS-80 such as the mismatch at the zero-salinity limit were largely resolved, with the exception of absolute internal consistency. A shortcoming in the work was that the effect of pressure was largely neglected. Seawater properties were defined solely as functions of temperature and salinity. The pressures were largely atmospheric except for temperatures greater than the atmospheric boiling point where the pressure was the vapor pressure of seawater.

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However, the correlations were accurate and were widely adopted across the engineering and desalination academia and industries.

Subsequently, in 2014, IAPWS released an industrial formulation of seawater referred here as IAPWS-14. IAPWS-14 was a modified version of IAPWS-08 that was 100-200 times computationally faster [4]. The increase in computation speed was achieved by changing how the pure water part of IAPWS-08 was computed. Instead of using IAPWS-95, the pure water equation of state for "general and scientific use", IAPWS-IF97, the industrial formulation for "industrial use" was used. The increase in computational speed came with a very small reduction in the accuracy of IAPWS-14 when compared to that of IAPWS-08. A shortcoming in both IAPWS-08 and IAPWS-14 is that due to the lack of experimental data of seawater density, they do not reliably predict seawater properties at elevated pressures beyond the oceanographic range of temperature and salinity ($0 \leq t \leq 40$ °C, $0 \leq S \leq 42$ g/kg). Authors of IAPWS-14 have explicitly mentioned that "no statements can be made about the accuracy at high pressures for temperatures greater than 313 K and salinities greater than 42 g/kg". This is primarily because both IAPWS-08 and IAPWS-14 are polynomial fit to datasets. When these functions are extrapolated beyond the range of experimental data, significant error could arise from over-fitting.

In this paper, a methodology based on thermodynamics is proposed to predict the pressure dependence of important seawater properties; selected correlations for engineering applications previously developed by Sharqawy et al. [2] are modified to include pressure dependence; new easy-to-use and more accurate correlations were proposed for seawater vapor pressure and Gibbs

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energy; and a review of recent work on seawater properties such as density, surface tension, thermal conductivity and osmotic coefficient, is presented.

Key to predicting the pressure dependence of important seawater properties was the observation that isothermal compressibility was linear with salinity— an approximation which is justified later in this paper. This allows the linear extrapolation of isothermal compressibility of seawater in the regions where experimental data are not present. Uncertainty bounds are estimated by statistical methods and by comparing seawater property predictions with those for aqueous sodium chloride. The pressure dependence of seawater density, isobaric expansivity, specific heat capacity, enthalpy, entropy and Gibbs energy, are then obtained using thermodynamic identities. Correlations are made that capture just the effect of pressure. These are added to the pressure-independent correlations made by Sharqawy et al. [2] to obtain simple polynomial correlations that were functions of temperature, salinity, and pressure. The final correlations are all valid for the typical range of desalination operation: $10 \leq t \leq 120\ °\mathrm{C},\ 0 \leq S \leq 120$ g/kg and $0 \leq P \leq 12$ MPa, with select properties being valid across a larger range of temperature and salinity.

The term "maximum uncertainty" is used to characterize the uncertainty between values calculated from correlations developed in this paper and the actual value of the property. There are two aspects to the maximum uncertainty. Experimental data used in developing correlations have an uncertainty [25] associated with them. Further, deviations exist between the experimental data and the value calculated by the correlation fit to the data. In this paper, "maximum uncertainty" for a correlation ($U_{\max}$) is defined as:

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$$U_{\text{max}} = \max\left(U_{\text{max, exp.}}, MAPD\right) \tag{1}$$

where, $U_{\text{max, exp.}}$ is the maximum uncertainty in the experimental data used to make a correlation and, $MAPD$ is defined as the maximum percentage absolute deviation between experimental data and the correlation value:

$$MAPD = \max\left(\left|\frac{X_{\text{data},i} - X_{\text{fit},i}}{X_{\text{fit},i}}\right| \times 100\right) \tag{2}$$

For some correlations such as Gibbs energy, the value of the correlation approaches zero within the desalination range of temperature and salinity. This causes a singularity for $MAPD$ which distorts the analysis of a correlation. In such cases, a more appropriate definition of "maximum uncertainty" is the maximum absolute deviation (MAD) between experimental data and the correlation value:

$$MAD = \max\left(\left| X_{\text{data},i} - X_{\text{fit},i} \right|\right) \tag{3}$$

2. Vapor pressure

In 2010, Sharqawy et al. [2,26] presented a review of past seawater vapor pressure studies and an expression for seawater vapor pressure based on Raoult's law. Raoult's law assumes that the solution is ideal and can be quite inaccurate at high salinities due to increased non-idealities in seawater [27,28]. For better quantifying the error and to investigate whether a more accurate expression could be developed, experimental datasets in the literature on seawater vapor pressure

were analyzed. Datasets by Robinson [29], Emerson and Jamieson [30] and Grunberg [31] are outlined in Table 2.

For quantifying the error in using Raoult's law, percentage deviations were evaluated between literature data on seawater vapor pressure and Sharqawy et al.'s expression. Figure 1 shows the percentage deviation of seawater vapor pressure as a function of salinity. The deviation can be as high as 2.5 % at a salinity of 160 g/kg.

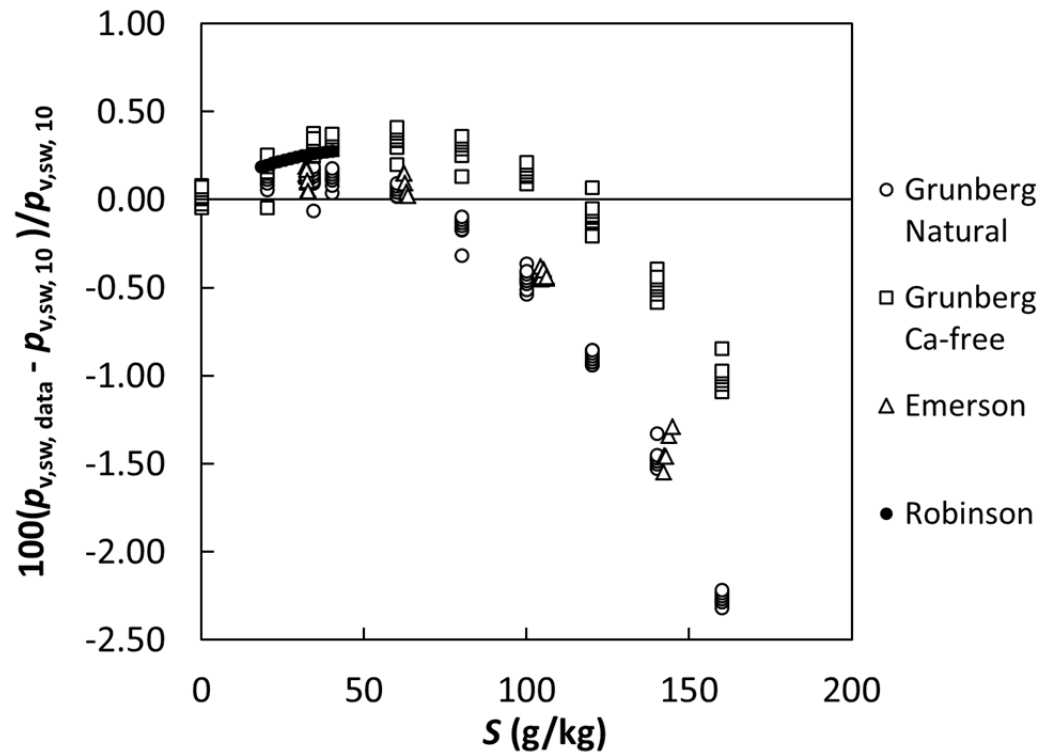**Figure 1.** Deviation of literature data on vapor pressure of seawater from the expression presented by Sharqawy et al. in 2010 [2]

In the present work, a newer and more accurate correlation for the vapor pressure of seawater as a function of salinity and temperature is developed. For consistency with the standard SI units, salinity and temperature in all datasets from literature were converted into

"Reference Salinity" and ITS-90 scales respectively. Two sets of data: primary and secondary, were used for developing the correlation. Primary data was used to generate the correlation while secondary data was used to compare to the correlation.

A summary of measurements of seawater vapor pressure from literature used in developing the correlation is given in Table 1. Measurements from Grunberg for natural seawater were used as primary data since Grunberg's data extended over a wide range of temperature and salinity. Natural seawater was selected as most experimental studies [5,32–34] for high salinity seawater used seawater containing calcium with the precipitation of calcium being suppressed in experiments through pH control. Only studies conducted by the National Engineering Laboratory (NEL) [30,31,35] used "Ca-free" artificial seawater. For these studies, a separate correlation was developed using Grunberg's artificial seawater data described in Appendix C.

Table 1. Data for seawater vapor pressure.

Ref.	Year	Seawater type	t (°C)	S (g/kg)	$u_c(p_v)/p_v$ (%)
Primary					
Grunberg [31]	1970	Natural	20–180	0–160	0.07
Secondary					
Robinson [29]	1954		25	18–40	0.02
Emerson [30]	1967	Synthetic	100–180	32–145	0.07

Grunberg [31]	1970	Ca-free	20–180	0–160	0.07
Bromley [33]	1974	Natural	0-20	0-160	
Sharqawy[2]	2010	Raoult's Law			

The best-fit correlation for the vapor pressure of natural seawater is given in Table 2. The correlation is valid across a temperature range of $t = (0 - 180)$ °C and a salinity range of $S = (0 - 160)$ g/kg. The maximum absolute deviation from primary data was 0.26 % while the average absolute deviation was 0.06 %. The deviations from Grunberg's data as well as other datasets are depicted in Figure 2. At high salinities, the data from Emerson and Jamieson [30] deviates by maximum of 0.35 %. This may be attributed to the "Ca-free" artificial seawater used by Emerson and Jamieson. Robinson's data fits well within the maximum deviation of the correlation.

Experimental data on the vapor pressure of seawater is unavailable for temperatures less than 20 °C. However, to estimate the maximum uncertainty of extrapolating the correlation to 0 °C, vapor pressure calculated using Eq. (5) was compared to vapor pressure calculated from activity coefficient data published by Bromley et al. [33]. Activity coefficient data in the temperature range of $t = (0\text{-}20)$ °C and salinity range of $S = (0\text{-}160)$ g/kg was used to obtain vapor pressure using the thermodynamic formulation:

$$p_{v,sw} = a_{w,sw} \times p_{v,w}. \tag{4}$$

where $a_{w,sw}$ is the activity of water in seawater. Bromley had calculated the activity of water in seawater using a thermodynamic model fit to experimental data on the boiling point elevation of seawater. The maximum deviation of vapor pressure calculated from Bromley's data was 0.91 %. Given the absence of any other dataset apart from Bromley's calculated values, the

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conservative estimate of the maximum uncertainty of the extrapolation of Eq. (5) for $t = (0\text{-}20)$ °C was assumed to be 0.91 %.

Table 2. Seawater vapor pressure correlations.

Equations:

$p_{\text{v sw}}$ in Pa, T in K and S in g/kg;

$$\ln\left(p_{v,sw} / p_{v,w}\right) = -4.58180 \times 10^{-4} S - 2.04430 \times 10^{-6} S^2 \tag{5}$$

where,

$$\ln\left(p_{v,w}\right) = a_1 / T + a_2 + a_3 T + a_4 T^2 + a_5 T^3 + a_6 \ln(T) \tag{6}$$

$a_1 = -5800, a_2 = 1.3915, a_3 = -4.8640 \times 10^{-2}, a_4 = 4.1765 \times 10^{-5},$
$a_5 = -1.4452 \times 10^{-8}, a_6 = 6.5460$

Range of validity and maximum uncertainty:

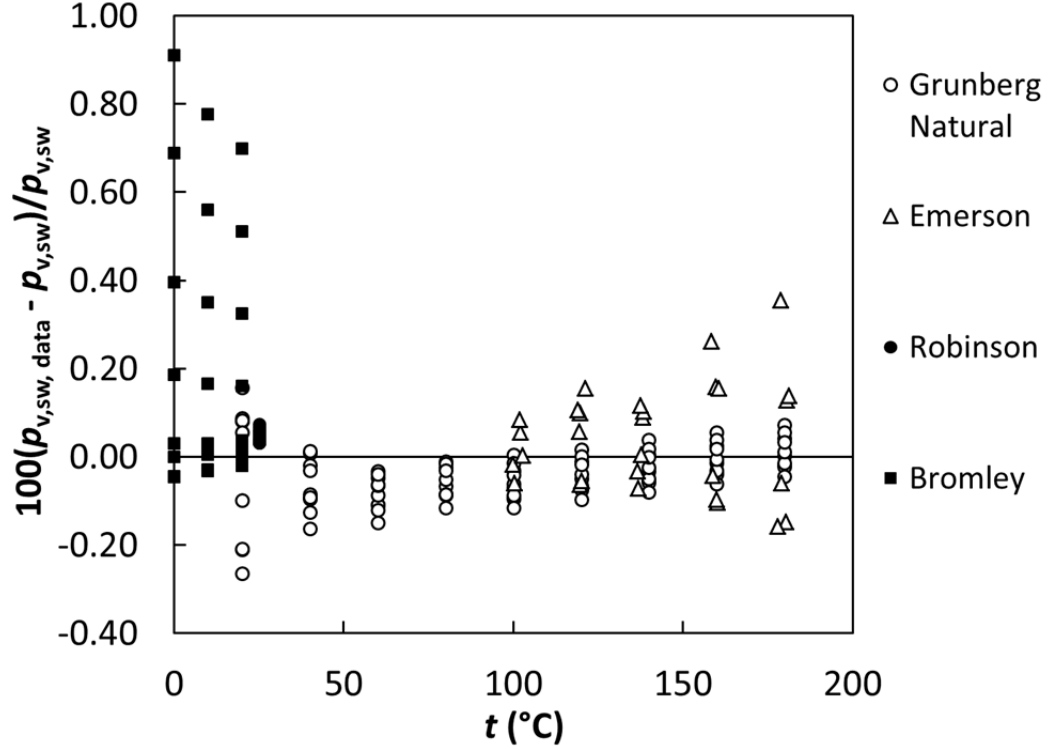|	Range	U_{max}
Primary data	$0 \leq t \leq 180$ °C; $0 \leq S \leq 160$ g/kg	±0.26 %
	Ref: [31]	
Extrapolation	$0 \leq t \leq 20$ °C; ; $0 \leq S \leq 160$ g/kg;	±0.91 %
	Ref: [33]	

Figure 2. Deviation of Eq. (5) from literature data on vapor pressure of natural seawater.

3. Methodology for evaluating pressure dependence

Experimental data for seawater thermophysical properties at elevated pressures ($P > 0.2$ MPa) is limited. However, fundamental thermodynamic relationships can be applied to express seawater properties like specific heat capacity, enthalpy and entropy at any pressure as a thermodynamic function of the value of the corresponding property at or near atmospheric pressure and the pressure-dependent seawater volumetric data as follows:

$$f(t,S,P) = f(t,S,P_0) + \int_{P_0}^{P} g\left(\kappa_{T,\text{sw}}, \beta_{P,\text{sw}}\right) dP \qquad (7)$$

In Eq. (10), $f(t, S, P)$ represents the value of a generic seawater thermophysical property at any temperature, t, salinity, S, and pressure, P. The function $f(t, S, P_0)$ represents seawater

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thermophysical properties correlated in 2010 by Sharqawy et al. across the same temperature and salinity range but restricted to pressure P_0 given by

$$P_0 = \begin{cases} P_{\text{atm}} = 0.101 \text{ MPa}, & \text{if } t \leq 100°C \\ P_{\text{v,sw}}(t,S) & \text{otherwise} \end{cases} \tag{8}$$

where, $P_{\text{v,sw}}(t,S)$ is the vapor pressure of seawater, from Eq. (5), in units of MPa.

The function $g\left(\kappa_{T,\text{sw}}, \beta_{P,\text{sw}}\right)$ represents a thermodynamic function of $\kappa_{T,\text{sw}}$, the isothermal compressibility [36] of seawater at constant composition

$$\kappa_{T,\text{sw}} = \frac{1}{\rho_{\text{sw}}}\left(\frac{\delta\rho_{\text{sw}}}{\delta P}\right)_{T,S} = -\frac{1}{v_{\text{sw}}}\left(\frac{\delta v_{\text{sw}}}{\delta P}\right)_{T,S}; \tag{9}$$

and $\beta_{P,\text{sw}}$, the isobaric thermal expansivity [36] of seawater at constant composition:

$$\beta_{P,\text{sw}} = -\frac{1}{\rho_{\text{sw}}}\left(\frac{\delta\rho_{\text{sw}}}{\delta T}\right)_{P,S} = \frac{1}{v_{\text{sw}}}\left(\frac{\delta v_{\text{sw}}}{\delta T}\right)_{P,S}. \tag{10}$$

The generic relationship expressed in Eq. (7) is expanded in Table 3 to show expressions for the pressure dependence of density, specific heat capacity, enthalpy, and entropy. These expressions were directly derived from thermodynamic identities given in the literature [36]. In all the integrands in Table 3, only pressure is varied while temperature and salinity are held constant. To evaluate the pressure dependence of seawater properties in the desalination range of temperature and salinity, the isothermal compressibility of seawater across the desalination range must first be obtained. This is discussed in Sec. 4. The pressure-dependent density of seawater in the desalination range can then be obtained using the thermodynamic relationship given in Eq. (11). Subsequently, other thermophysical properties of seawater can be evaluated using Eqs. (12)–(15).

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Table 3. Expressions representing the pressure dependence of seawater properties as a function of properties at a known pressure and seawater volumetric properties; derived from [36]

$$\rho_{sw}\left(T,S,P\right)=\rho_{sw}\left(T,S,P_0\right)\exp\left(\int_{P_0}^{P}\kappa_{T,sw}dP\right) \tag{11}$$

$$
\begin{aligned}
c_{P,sw}\left(t,S,P\right) &= c_{P,sw}\left(T,S,P_0\right)-\int_{P_0}^{P}T\left(\frac{\partial^2 \upsilon_{sw}}{\partial T^2}\right)_{P,S}dP \\
&= c_{P,sw}\left(t,S,P_0\right)-\int_{P_0}^{P}T\left(\frac{2}{\rho_{sw}^{3}}\left(\frac{\partial\rho_{sw}}{\partial T}\right)^2-\frac{1}{\rho_{sw}^{2}}\frac{\partial^2\rho_{sw}}{\partial T^2}\right)_{P,S}dP
\end{aligned}
\tag{12}
$$

$$h_{sw}\left(T,S,P\right)=h_{sw}\left(T,S,P_0\right)+\int_{P_0}^{P}\upsilon_{sw}\left(1-\beta_{P,sw}T\right)dP \tag{13}$$

$$g_{sw}\left(T,S,P\right)=g_{sw}\left(T,S,P_0\right)+\int_{P_0}^{P}\upsilon_{sw}dP \tag{14}$$

$$s_{sw}\left(T,S,P\right)=s_{sw}\left(T,S,P_0\right)-\int_{P_0}^{P}\left(\upsilon_{sw}\beta_{P,sw}\right)dP \tag{15}$$

4. Isothermal compressibility

The isothermal compressibility of seawater is required to evaluate the pressure dependence of seawater density, isobaric thermal expansivity and by extension other thermophysical properties. Several researchers have in the past derived it from measurements of either the

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density of seawater [5,37,38] or the speed of sound in seawater [39,40]. In 1969, Wilson [41] measured the speed of sound in seawater across a temperature range of -4 to 30 °C, a salinity range of 0–37 g/kg and a pressure range of 0.1–100 MPa and developed a correlation that fit the measurement to within a standard deviation of 0.30 m/s. These measurements were used by Wang and Millero [39] in 1973 to determine the compressibility of seawater to within a maximum error of 2×10^{-7} MPa^{-1} (≈ 0.05 %). In 1976, Chen and Millero [42] determined the compressibility of seawater by measuring the specific volume of seawater across a temperature range of 0–40 °C, a salinity range of 5–40 g/kg and a pressure range of 0.1–100 MPa. The deviation between their compressibility values and that of Wang and Millero was within 0.05 %.

Recently, Millero and Huang [40] measured the speed of sound in seawater at atmospheric pressure across a temperature range of 0–95 °C and an absolute salinity range of 0–50 g/kg to a precision of 0.12 m/s. The measurements were then used to correlate the compressibility of seawater. The correlation has a standard deviation of 5.8×10^{-8} MPa^{-1} (≈ 0.01 %). The data for isothermal compressibility was subsequently used by Rodriguez [43] to generate a new correlation for seawater isothermal compressibility that had a standard deviation of 2.7×10^{-8} MPa^{-1}. Safarov et al. measured the density of seawater accurately to within an uncertainty of 0.03 % across a wide range of pressure and temperature ($0.1 \leq P \leq 140$ MPa and $0 \leq t \leq 195 °C$) for salinities of 35 g/kg [38], 32–56 g/kg [5] and 3–30 g/kg [37] and, developed a new equation of state for seawater [5] that fit their 7616 measurements to within 0.08 %. The equation of state was then used by Safarov et al. to accurately obtain the isothermal compressibility of seawater as well as other seawater volumetric properties. Compressibility computed from Safarov et al.'s equation agreed with the results of Chen and Millero to within 3.4×10^{-6} MPa^{-1} (≈ 0.85 %).

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Experimental data for the isothermal compressibility of seawater is available up to a salinity of 56 g/kg. To evaluate the pressure dependence of seawater properties in the desalination range of temperature and salinity, an estimation of the isothermal compressibility of seawater beyond a salinity of 56 g/kg is required. In the present work, an engineering approximation was used for this purpose—expressing compressibility as a linear function of salinity, fitting the function to known data and then extrapolating the function to high salinities $(56 < S \leq 160$ g/kg). This was possible because isothermal compressibility of seawater was found to vary approximately linearly with salinity at a constant temperature and pressure as shown in Fig. 3. This approach of using a linear variation in salinity was earlier used by Sun et al. [44] to estimate the density and specific heat capacity of seawater at high salinities.

Two important questions regarding the approximation mentioned above must be answered for a comprehensive analysis. First, how accurate is the linear approximation of the isothermal compressibility of seawater? Second, given the linear approximation, what is the maximum deviation from the correlation when the expression is extrapolated beyond 56 g/kg? To address the first question of validity of the linear approximation, isothermal compressibility data for aqueous sodium chloride published by Rogers and Pitzer [45] was analyzed. Unlike seawater, the data for aqueous sodium chloride extends to high salinities (S = 226 g/kg or molality m = 5 mol/kg) and since sodium chloride is the primary constituent of seawater, the behavior of aqueous sodium chloride can be a good indicator for seawater. The analysis is described at length in Appendix A.1. To address the second question of estimating the maximum uncertainty of the fitted function in the region of extrapolation, a detailed statistical analysis was performed. The analysis is described in Appendix A.2.
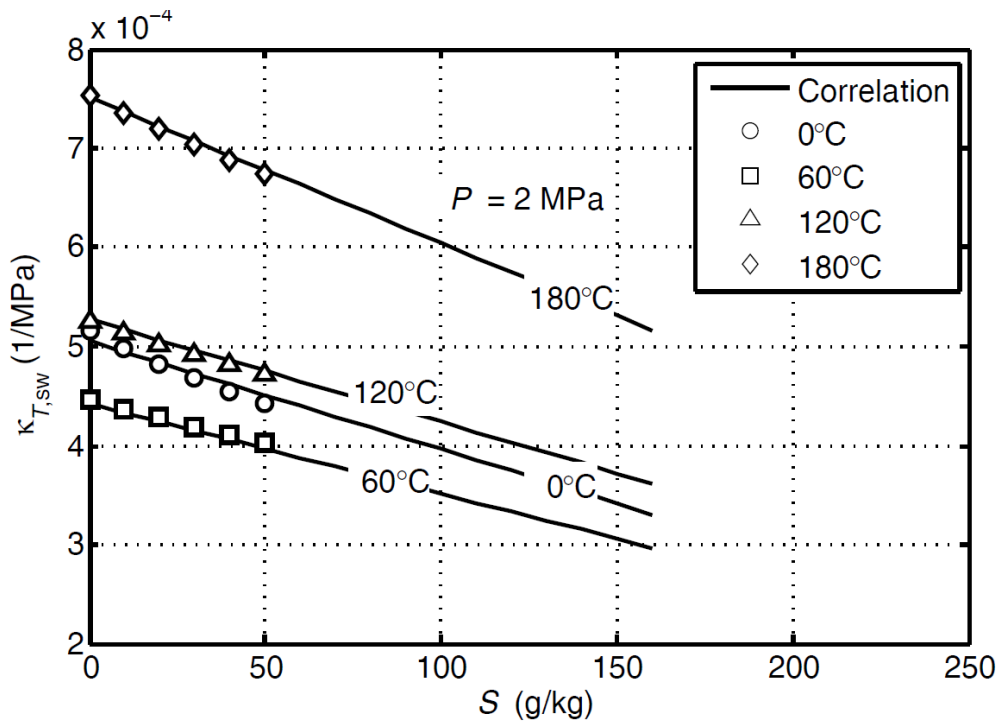
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Figure 3. Comparison of seawater isothermal compressibility smoothed data from Safarov et al. [5,37] with values from the correlation given in Eq. (16) across salinities 0–160 g/kg at temperatures 0, 60, 120 and 180 °C and at a pressure of 2 MPa.

The isothermal compressibility of seawater was expressed as a sum of pure water isothermal compressibility and a 4-term saline part which was linear in salinity. Table 4 summarizes the compressibility data used to develop the correlation for the isothermal compressibility of seawater along with the combined standard uncertainties of the original experimental measurements of density or the speed of sound used to compute compressibility. Primary data for generating the pure water isothermal compressibility correlation came from the IAPWS-95 formulation for pure water [46] across a temperature range of 0–180 °C and pressure range of 6×10^{-4}–12 MPa. Primary data used for correlating the saline part came from data

published by Safarov et al. [5,37] for temperatures 0–195 °C, salinities 3–56 g/kg and pressures 0.2–21 MPa. The data from Safarov et al. was preferred over other sources because of the wide range of temperatures, salinities and pressures it was valid for, and also because of the high accuracy of their density measurements and of the fit that was used. The final correlation is given in Eq. (16). The percentage deviation between the data of Safarov et al. and compressibility calculated using Eq. (16) is depicted in Fig. 4. The average absolute deviation and the maximum absolute deviation between the data and the correlation are also listed in Table 4. The maximum absolute deviation from the primary data was 3.47 % at $t = 0$ °C and $S = 56$ g/kg from Safarov et al.'s 2013 work. This was taken to be the maximum uncertainty of Eq. (16) within the range of the primary data. Please see Table 5 for a summary of the correlation for isothermal compressibility of seawater, its validity region and its maximum uncertainty.

To obtain the maximum uncertainty in the region of extrapolation, the maximum uncertainty in the correlation at $S = 56$ g/kg was propagated to $S = 160$ g/kg. This was possible because of the linear variation of isothermal compressibility with salinity. As mentioned previously, the detailed analysis can be found in Appendix A.2. The maximum absolute deviation in the region of extrapolation was estimated to be 13.36 % at $t = 0$ °C, $S = 160$ g/kg and $P = 20$ MPa. This was taken to be the maximum uncertainty of Eq. (16) within the region of extrapolation.

The variation of isothermal compressibility of seawater, calculated from Eq. (16), with temperature and salinity at pressure $P = 6$ MPa in the region of primary data (solid lines) and in

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the region of extrapolation (dashed line) is shown in Fig. 5. It can be clearly seen that the extrapolation is smooth without instabilities from overfitting.

Table 4. Data sources used to develop a correlation for seawater isothermal compressibility in this work.

Ref.	Year	Seawater type	t (°C)	S (g/kg)	P (MPa)	$u_c(\rho)/\rho$ (%)	AAPD[a] (%)	MAPD[b] (%)
Primary data								
IAPWS [46]	1995	Pure water	0–180	0	6×10^{-4}–12	0.01	0.09	0.29
Safarov [5]	2012	IAPSO	0–195	32–56	0.5–21	0.03	0.58	3.47
Safarov [37]	2013	IAPSO	0–195	3–30	0.2–21	0.03	0.78	2.23
Secondary data								
Rodriguez [43]	2012		0–95	0–50	0.1	0.01^{c}	0.74	2.33

a: AAPD – average absolute percentage deviation of data from correlation

b: MAPD – maximum absolute percentage deviation of data from correlation

c: speed of sound in seawater

Table 5. Seawater isothermal compressibility correlation.

Equations:
$\kappa_{T,sw}$ in MPa^{-1}, t in °C, S in g/kg and P in MPa;

$$\kappa_{T,sw} = \kappa_{T,w} + S \times (b_1 + b_2 t + b_3 t^2 + b_4 P) \tag{16}$$

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where,

$$\kappa_{T,w} = a_1 + a_2 t + a_3 t^2 + a_4 t^3 + a_5 t^4 + a_6 t^5 + P \times (a_7 + a_8 t + a_9 t^3) \qquad (17)$$

$a_1 = 5.0792 \times 10^{-4}, a_2 = -3.4168 \times 10^{-6}, a_3 = 5.6931 \times 10^{-8}, a_4 = -3.7263 \times 10^{-10},$
$a_5 = 1.4465 \times 10^{-12}, a_6 = -1.7058 \times 10^{-15}, a_7 = -1.3389 \times 10^{-6}, a_8 = 4.8603 \times 10^{-9},$
$a_9 = -6.8039 \times 10^{-13}$

$b_1 = -1.1077 \times 10^{-6}, b_2 = 5.5584 \times 10^{-9}, b_3 = -4.2539 \times 10^{-11}, b_4 = 8.3702 \times 10^{-9}$

Range of validity and maximum uncertainty:

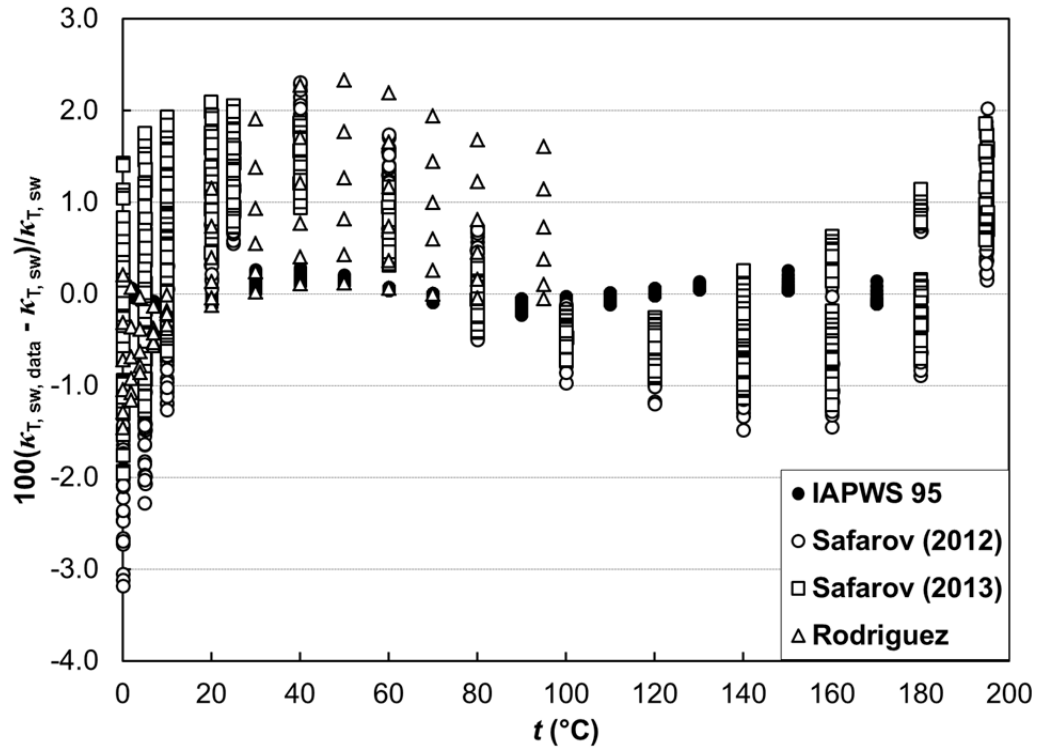|	Range	U_{max}
Primary data	$0 \leq t \leq 180$ °C; $0 \leq S \leq 56$ g/kg; $0 \leq P \leq 12$ MPa; Ref: [5,37,46]	±3.47 %
Extrapolation	$0 \leq t \leq 180$ °C; $56 < S \leq 160$ g/kg; $0 \leq P \leq 12$ MPa;	±13.36 %

Figure 4. Deviation of seawater isothermal compressibility data of Safarov et al. [5,37], Rodriguez, and Millero [43] from compressibility calculated using Eq. (16).
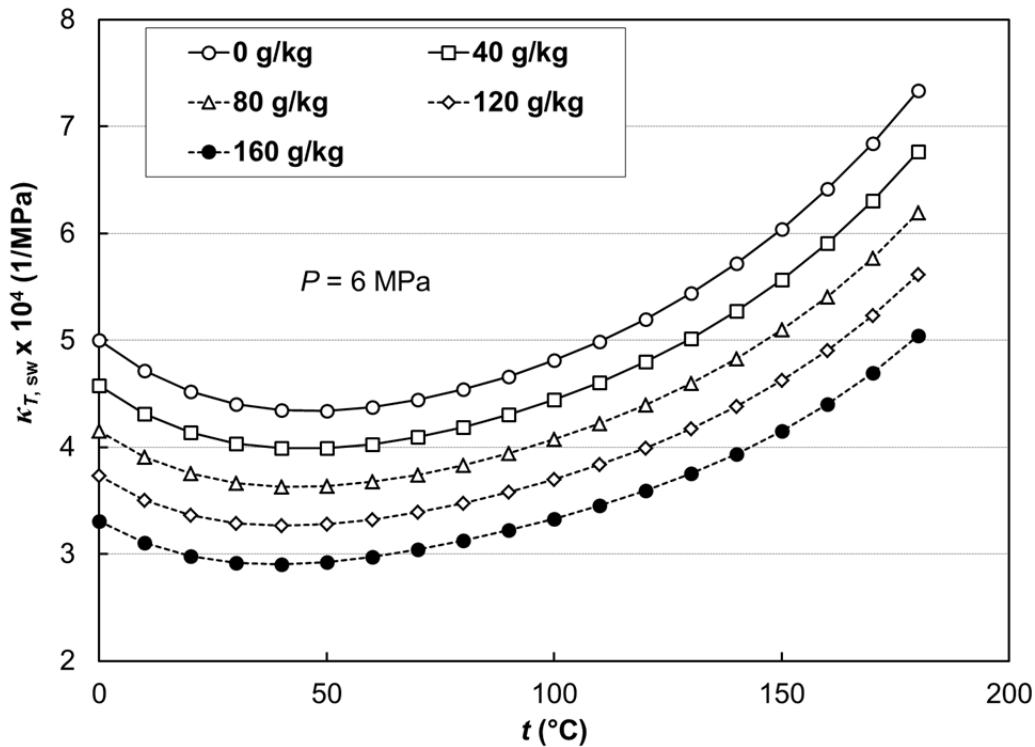
Figure 5. Variation of isothermal compressibility of seawater calculated using Eq. (16) with temperature and salinity at pressure $P = 6$ MPa. Solid lines represent the region of primary data while the dashed line represents the region of extrapolation.

5. Density

In 2010, Sharqawy et al. [2] presented a review of past literature on the density of seawater in the desalination range. The study also presented a new correlation for the density of seawater that fit the datasets of Isdale and Morris [35] and Millero and Poisson [22] to within a maximum deviation of ± 0.1 %. The correlation expressed density solely as a function of temperature and salinity for temperatures 0–180 °C and salinities 0–160 g/kg with the pressure being implicitly

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defined to be atmospheric for temperatures less than 100 °C and the vapor pressure of seawater for higher temperatures till 180 °C.

Since the review by Sharqawy et al., new measurements for seawater density were reported by Millero and Huang [47] and Safarov et al. [5,37]. Millero and Huang measured the density of seawater at atmospheric pressure for temperatures 0–90 °C and salinities 5–70 g/kg to within an estimated uncertainty of 0.006 kg/m^3 and fit the data to within a standard error of 0.0063 kg/m^3. Safarov et al. reported density measurements of seawater for: temperatures 0–195 °C, pressures up to 140 MPa and salinities 32–56 g/kg [5] (in 2012) and 3–30 g/kg [37] (in 2013) to within a reproducibility of 0.03 %. Previous studies that measured or evaluated seawater density at elevated pressures, were restricted to salinities of 42 g/kg and temperatures of 40 °C [39,42]. Measurements by Safarov et al. [5,37,38] are thus the best available seawater density measurements that accurately cover a wide range of temperature and pressure $0 \leq t \leq 195°C$ and $0.1 \leq P \leq 140$ MPa). However, even these measurements are restricted to a salinity of 56 g/kg.

To evaluate the density of seawater where experimental data does not exist ($P > 0.2$ MPa and $S > 56$ g/kg), the thermodynamic relationship between compressibility and density described in Eq. (11) was used. Isothermal compressibility of seawater was obtained from Eq. (16) while the density of seawater near atmospheric pressures, given in Eq. (19), was obtained from Sharqawy *et al*. The resulting expression for the density of seawater, valid for temperatures 0–180 °C, for salinities 0–160 g/kg and for pressures 0–12 MPa, is given in Eq. (18). To verify the maximum uncertainty of Eq. (18) in the region where experimental data exists, density

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calculated using Eq. (18) was compared with the density data reported by Grunberg [31] and Safarov et al. [5,37] and the percentage deviations between them was plotted in Fig. 6. The maximum deviation and thus the maximum uncertainty of the correlation in the region of experimental data was 0.14 %. For determining the maximum uncertainty of the correlation in the extrapolated region, an error analysis was conducted by propagating the error in seawater density in Eq. (19) and the error in seawater compressibility in Eq. (16). The analysis gave a maximum deviation of 0.21 % in the extrapolated region. A summary of the correlation and its maximum uncertainty is given in Table 6.

To quantify the effect pressure has on seawater density, the percentage deviation in density due to pressure was evaluated by taking the difference between the density of seawater at any pressure P, given in Eq. (18), and the density of seawater at pressure P_0, given in Eq. (19), and normalizing it with the density of seawater at pressure P_0. The evaluated percentage deviation in density due to pressure is depicted in Fig. 7.

Table 6. Seawater density correlation.

Equations:
ρ_{sw} in kg/m^3, t in °C , S in g/kg and P in MPa;

$\rho_{sw}(t,S,P) = \rho_{sw}(t,S,P_0) \times F_P$	(18)
where,	
$\rho_{sw}(t,S,P_0) = \left(a_1 + a_2 t + a_3 t^2 + a_4 t^3 + a_5 t^4\right) +$ $\left(b_1 S_{kg/kg} + b_2 S_{kg/kg} t + b_3 S_{kg/kg} t^2 + b_4 S_{kg/kg} t^3 + b_5 S_{kg/kg}^2 t^2\right)$	(19)

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$$a_1 = 9.999 \times 10^2, a_2 = 2.034 \times 10^{-2}, a_3 = -6.162 \times 10^{-3}, a_4 = 2.261 \times 10^{-5}, a_5 = -4.657 \times 10^{-8}$$

$$b_1 = 8.020 \times 10^2, b_2 = -2.001, b_3 = 1.677 \times 10^{-2}, b_4 = -3.060 \times 10^{-5}, b_5 = -1.613 \times 10^{-5}$$

$$S_{kg/kg} = S / 1000$$

is from Ref. [2] and,

$$F_P = \exp\left(\int_{P_0}^{P} \kappa_{T,sw} \, dP \right)$$

$$= \exp\left[\begin{matrix} (P - P_0) \times \left(c_1 + c_2 t + c_3 t^2 + c_4 t^3 + c_5 t^4 + c_6 t^5 + S \times (d_1 + d_2 t + d_3 t^2) \right) + \\ \dfrac{(P^2 - P_0^2)}{2} \times \left(c_7 + c_8 t + c_9 t^3 + d_4 S \right) \end{matrix} \right] \qquad (20)$$

$$c_1 = 5.0792 \times 10^{-4}, c_2 = -3.4168 \times 10^{-6}, c_3 = 5.6931 \times 10^{-8}, c_4 = -3.7263 \times 10^{-10},$$

$$c_5 = 1.4465 \times 10^{-12}, c_6 = -1.7058 \times 10^{-15}, c_7 = -1.3389 \times 10^{-6}, c_8 = 4.8603 \times 10^{-9},$$

$$c_9 = -6.8039 \times 10^{-13}$$

$$d_1 = -1.1077 \times 10^{-6}, d_2 = 5.5584 \times 10^{-9}, d_3 = -4.2539 \times 10^{-11}, d_4 = 8.3702 \times 10^{-9}$$

Range of validity and maximum uncertainty:

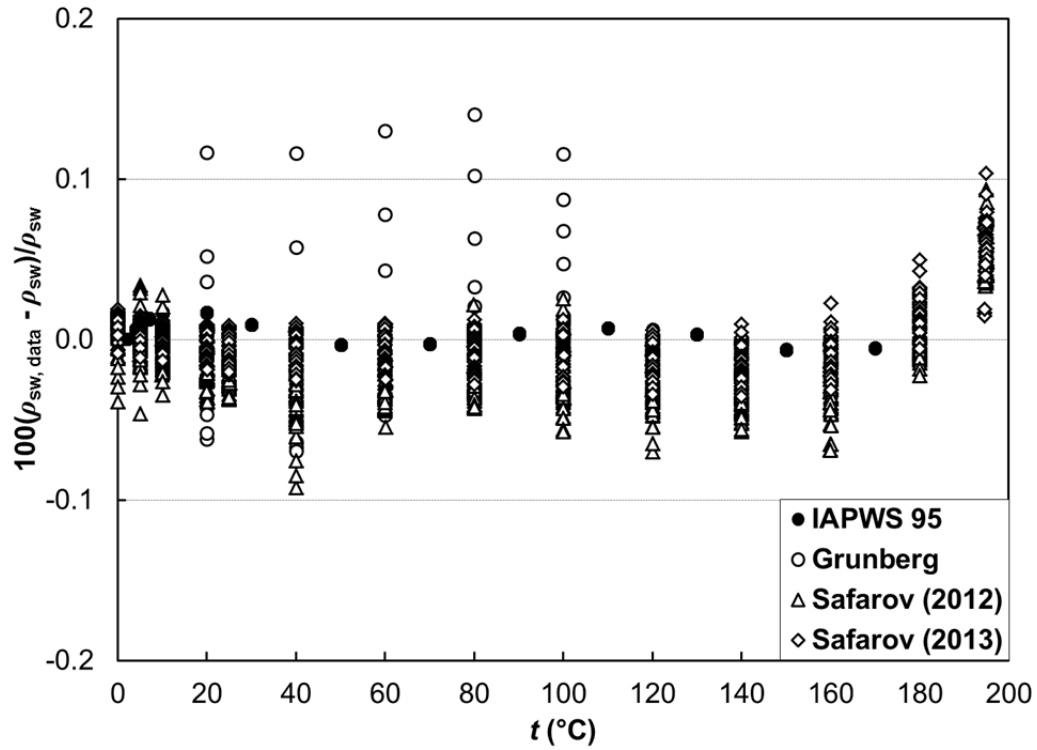|	Range	U_{max}
Primary data	$0 \le t \le 180$ °C; $0 \le S \le 150$ g/kg; $0.1 \le P = P_0 \le 1$ MPa;	±0.14 %
	$0 \le t \le 180$ °C; $0 \le S \le 56$ g/kg; $0.2 \le P \le 12$ MPa;	
	Ref: [5,22,35,37,46]	
Extrapolation	$0 \le t \le 180$ °C; $56 < S \le 150$ g/kg; $0 \le P \le 12$ MPa;	±0.21 %

Figure 6. Deviation of seawater density data of Grunberg [31] and Safarov et al. [5,37] from density calculated using Eq. (18).
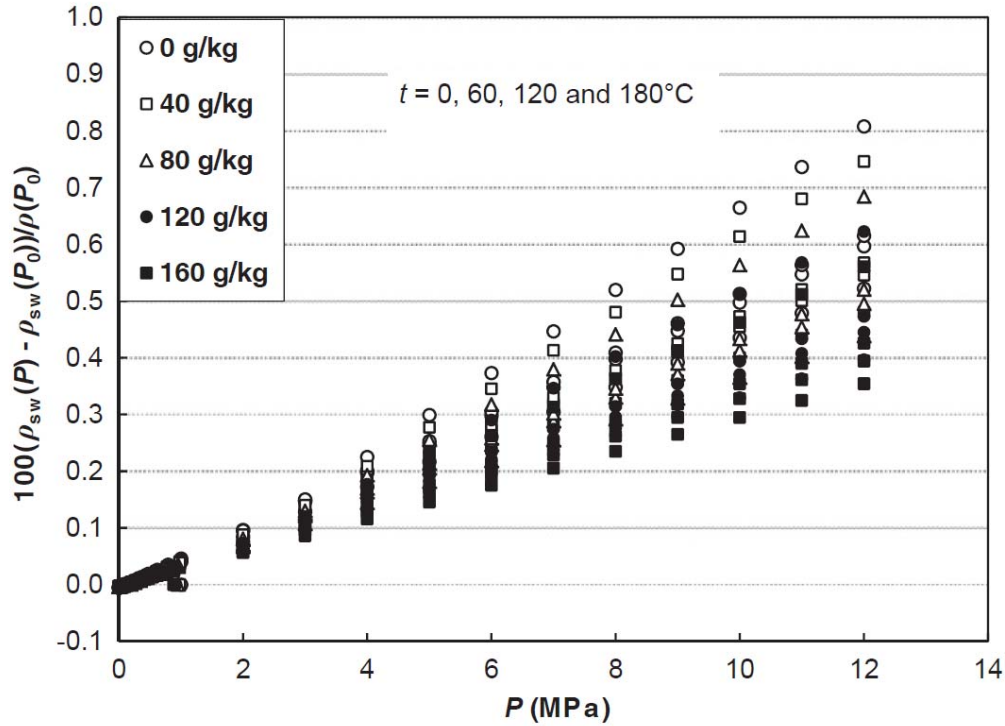
Figure 7. Variation of density of seawater with pressure calculated using Eq. (18) normalized with Eq. (19) for salinities $S = 0$, 40, 80, 120 and 160 g/kg at temperatures $t = 0$, 60, 120 and 180 °C.

6. Isobaric thermal expansivity

The isobaric thermal expansivity of seawater has been evaluated in the past for salinities up to 56 g/kg. In 1970, Bradshaw and Schneider [48] experimentally measured the expansivity of seawater for temperatures -2 to 30 °C, for reference salinities 30.6, 35.2 and 39.7 g/kg and for 0.8-100.1 MPa to an uncertainty of 3×10^{-6} 1/K. In 1976, Chen and Millero [42], evaluated the expansivity from measurements of specific volume of seawater, for temperatures 0-40 °C and for salinities 0-42 g/kg and up to a pressure of 100 MPa to an uncertainty of 2×10^{-6} 1/K. More recently, Safarov et al. [5,37] evaluated expansivity from density measurements of seawater, for

temperatures 0-195 °C, for salinities 0-56 g/kg and for pressures 0.1-140 MPa. Safarov et al.'s data agreed with past data of Chen and Millero to within 16 x 10^{-6} 1/K.

To evaluate the isobaric thermal expansivity of seawater in the desalination range, the thermodynamic relationship, given in Eq. (10), and the density of seawater given in Eq. (18) was used. The final expression is given in Eq. (21). For validating the final expression in the region of data, values calculated from Eq. (21) was compared with pure water data from IAPWS-95 and, seawater data from Safarov et al. [5,37]. Data from Safarov et al. was chosen over other authors due to the wide range of temperature, salinity and pressure represented. The percentage deviation between the data and the correlation is depicted in Fig. 8. The maximum deviation from seawater data was 11.37 % at 10 °C. For pure water, the deviation was lower at 8.76 %. Percentage deviations were found to increase for temperatures less than 10 °C because the denominator, thermal expansivity, approached zero near 4 °C. Thus, the validity region in temperature was restricted to 10 °C.

In the region of extrapolation, the deviation is not expected to be significantly higher since most of the deviation is in pure water part of the equation and at 10 °C. Analysis of isobaric expansivity data of aqueous sodium chloride from Rogers and Pitzer [45] showed that expansivity did not vary strictly linearly with salinity, especially at low temperature (< 20 °C). Thus, the approach of extrapolating uncertainty linearly with salinity as given in Section 4, cannot be applied to isobaric expansivity of seawater. However, an estimate of the maximum deviation at high salinity can be obtained by comparing the correlation with aqueous sodium chloride expansivity data from Rogers and Pitzer. The maximum deviation thus obtained, 18.30

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% at 10 °C and salinity of 150 g/kg (molality 3 mol/kg), was taken to be a good estimate of the uncertainty of Eq. (21) in the region of extrapolation. A summary of the correlation and its maximum uncertainty is given in Table 7.

The variation of isobaric expansivity of seawater, as calculated from Eq. (21), with temperature and salinity at a pressure of 60 MPa is shown in Fig. 9. The region of literature data is represented in by solid lines while dashed lines represent the region of extrapolation.

Table 7. Seawater isobaric thermal expansivity.

Equations:

β_{sw} in 1/K, t in °C, S in g/kg and P in MPa;

$$\beta_{sw}(t,S,P) = -\frac{1}{\rho_{sw}(t,S,P)} \left(\rho_{sw}(t,S,P_0) \left(\frac{\delta F_P}{\delta T} \right)_{S,P} + \left(\frac{\delta \rho_{sw}(t,S,P_0)}{\delta T} \right)_{S,P} F_P \right) \qquad (21)$$

where, $\rho_{sw}(t,S,P_0)$ is from Ref. [2] and given in Eq. (19) and, F_P is given in Eq. (20).

Range of validity and maximum uncertainty:

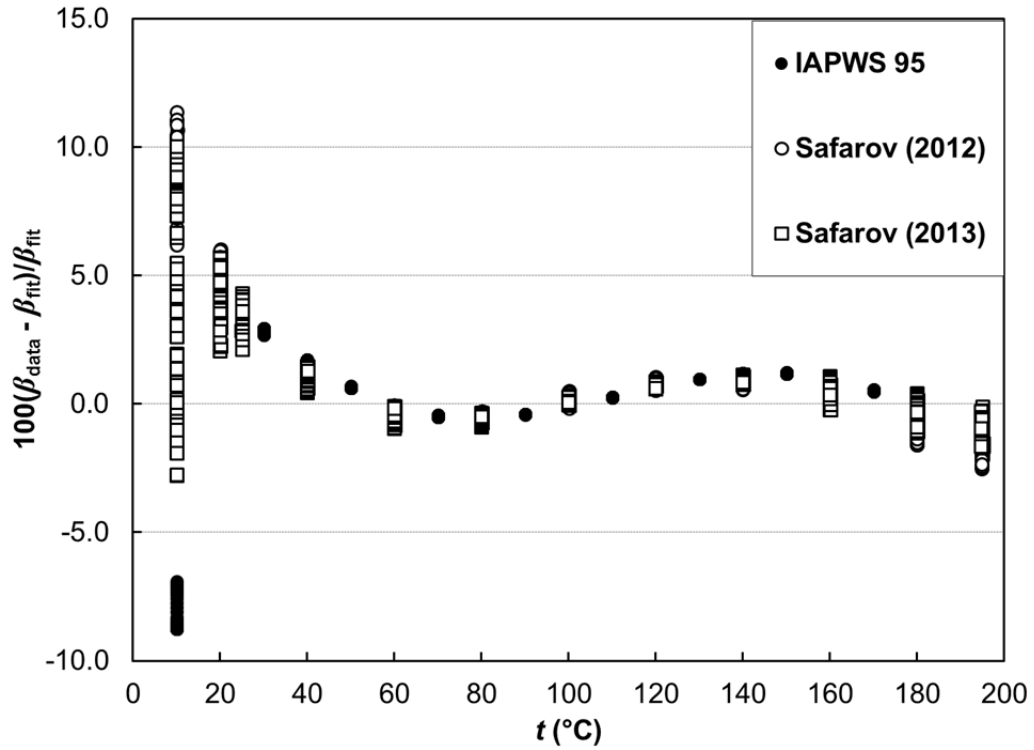|	Range	U_{max}
Literature data	$10 \leq t \leq 180$ °C; $S = 0$ g/kg; $0 \leq P \leq 12$ MPa;	±11.37 %
	$10 \leq t \leq 180$ °C; $0 \leq S \leq 56$ g/kg; $0.2 \leq P \leq 12$ MPa;	
	Ref: [5,37,46]	
Extrapolation	$10 \leq t \leq 180$ °C; $56 < S \leq 150$ g/kg; $0 \leq P \leq 12$ MPa;	±18.30 %

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Figure 8. Deviation of IAPWS-95 pure water expansivity data [46] and seawater

expansivity data of Safarov et al. [5,37] from expansivity calculated using Eq. (21).
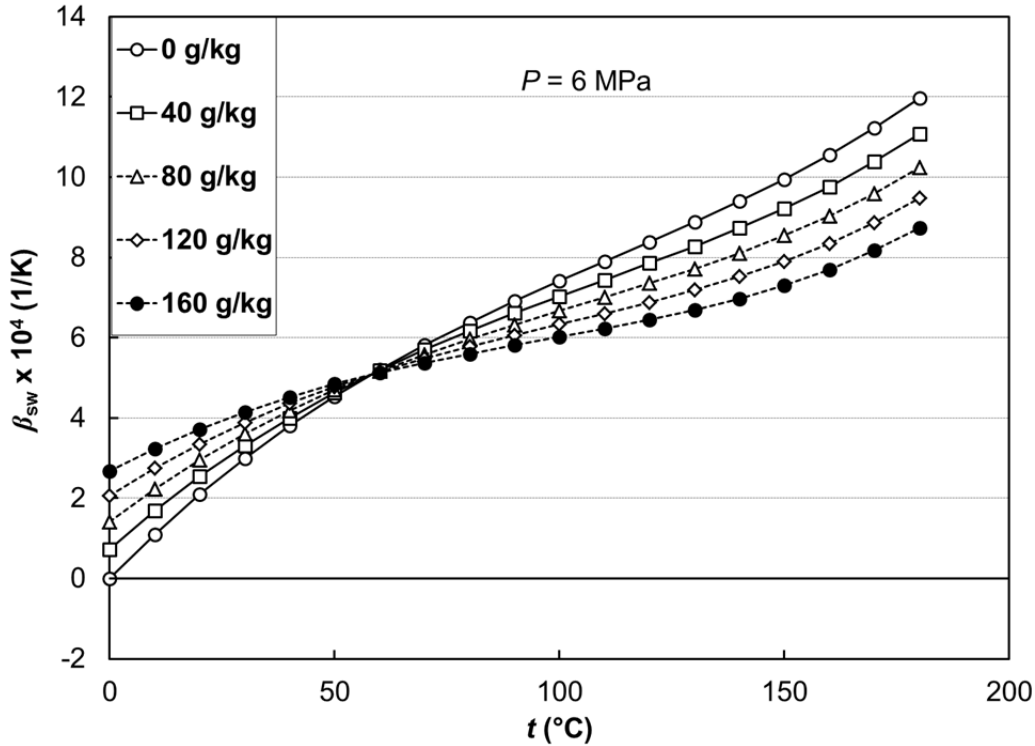
Figure 9. Variation of isobaric expansivity of seawater calculated using Eq. (21) with temperature and salinity at pressure $P = 6$ MPa. Solid lines represent the region of literature data while the dashed line represents the region of extrapolation.

7. Isobaric specific heat capacity

A review of past studies conducted on the specific heat capacity of seawater was given by Sharqawy et al. [2] in 2010. The studies were restricted to near atmospheric pressures. A correlation proposed first by Jamieson et al. [49] was recommended by Sharqawy et al. The original correlation was expressed as a function of the IPTS-68 temperature scale. In this paper, the same correlation is expressed as a function of the latest ITS-90 temperature scale without changing the coefficients in the correlation. This was because the increase in the maximum

percentage deviation of experimental data from the correlation, from not converting temperature scales, was just 0.02 %. The correlation had a maximum percentage deviation of 0.30 % while the uncertainty in Jamieson et al.'s measurements was 1 %. Thus, the actual uncertainty of the correlation was 1 %.

For evaluating specific heat capacity at high pressures (>0.2MPa), the thermodynamic relationship given in Eq. (12), the specific heat capacity at pressure P_0 given in Eq. (23) from Sharqawy et al. [2], and the density relationship seawater density correlation given in Eq.(18), were used. The evaluated specific heat capacities were then correlated to obtain a final expression given in Eq. (22). The equation is valid for temperatures 0–180 °C, for salinities 0–160 g/kg and for pressures 0–12 MPa. For validating the final expression at high pressures in the region of literature data, specific heat capacity at elevated pressures calculated from the correlation was compared with seawater specific heat capacity calculated from the IAPWS-08 equation of state for seawater, which accurately computes specific heat capacity along with its pressure dependence for temperatures 0–40 °C, for salinities 0–42 g/kg and for pressures 0–100 MPa, as well as with pure water specific heat capacity calculated from the IAPWS-95 equation of state for pure water which accurately computes specific heat capacity of liquid water along with its pressure dependence for temperatures 0–374 °C and for pressures 0–100 MPa. The percentage deviation between the data and the correlation is depicted in Fig. 10. The maximum deviation from data was 0.30 % at 0 °C. The deviation was higher than at 10 °C due to inaccuracy in the temperature derivative of seawater density for temperatures less than 10 °C. However, the deviations are smaller than the uncertainty of 1 % in the original measurements of Jamieson et al.. Analysis of the behavior of the final expression in the extrapolated region ($0 \leq t$

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$\leq 180\ °C; 42 \leq S \leq 160$ g/kg; $0 \leq P \leq 12$ MPa), showed that possible deviations were still within the 1 % overall uncertainty. This was further confirmed after evaluating the variation of specific heat capacity with pressure.

To quantify the effect pressure has on seawater specific heat capacity, the percentage deviation in specific heat capacity due to pressure was evaluated by taking the difference between the specific heat capacity of seawater at any pressure P, given in Eq. (22), and the specific heat capacity of seawater at pressure P_0, given in Eq. (23), and normalizing it with the specific heat capacity at pressure P_0. The evaluated percentage deviation in specific heat capacity due to pressure at different temperatures and salinities is depicted in Fig. 11. Specific heat capacity reduced by a maximum of 1.2 % at 12 MPa for pure water. The effect of pressure on specific heat capacity was found to decrease with salinity. The effect of pressure on seawater specific heat capacity was small and was approximately within the maximum uncertainty of the correlation. A summary of the correlation and its maximum uncertainty is given in Table 8.

Table 8. Seawater specific heat capacity.

Equations:

$c_{P,\mathrm{sw}}$ in J/kg K, t in °C, S in g/kg and P in MPa;

$$c_{P,\mathrm{sw}}(t,S,P)=c_{P,\mathrm{sw}}(t,S,P_0)+(P-P_0)\times(a_1+a_2 t+a_3 t^2+a_4 t^3+S\times(a_5+a_6 t+a_7 t^2+a_8 t^3))\ (22)$$

where, $c_{\mathrm{sw}}(t,S,P_0)$ is from Ref. [2] and given by:

$$c_{P,\mathrm{sw}}(t,S,P_0)=A+B(t+273.15)+C(t+273.15)^2+D(t+273.15)^3 \qquad (23)$$

and,

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$a_1 = -3.1118, a_2 = 0.0157, a_3 = 5.1014 \times 10^{-5}, a_4 = -1.0302 \times 10^{-6},$

$a_5 = 0.0107, a_6 = -3.9716 \times 10^{-5}, a_7 = 3.2088 \times 10^{-8}, a_8 = 1.0119 \times 10^{-9}$

$A = 5328 - 9.76 \times 10^1 S + 4.04 \times 10^{-1} S^2$

$B = -6.913 + 7.351 \times 10^{-1} S + 3.15 \times 10^{-3} S^2$

$C = 9.6 \times 10^{-3} - 1.927 \times 10^{-3} S + 8.23 \times 10^{-6} S^2$

$D = 2.5 \times 10^{-6} + 1.666 \times 10^{-6} S - 7.125 \times 10^{-9} S^2$

Range of validity and maximum uncertainty:

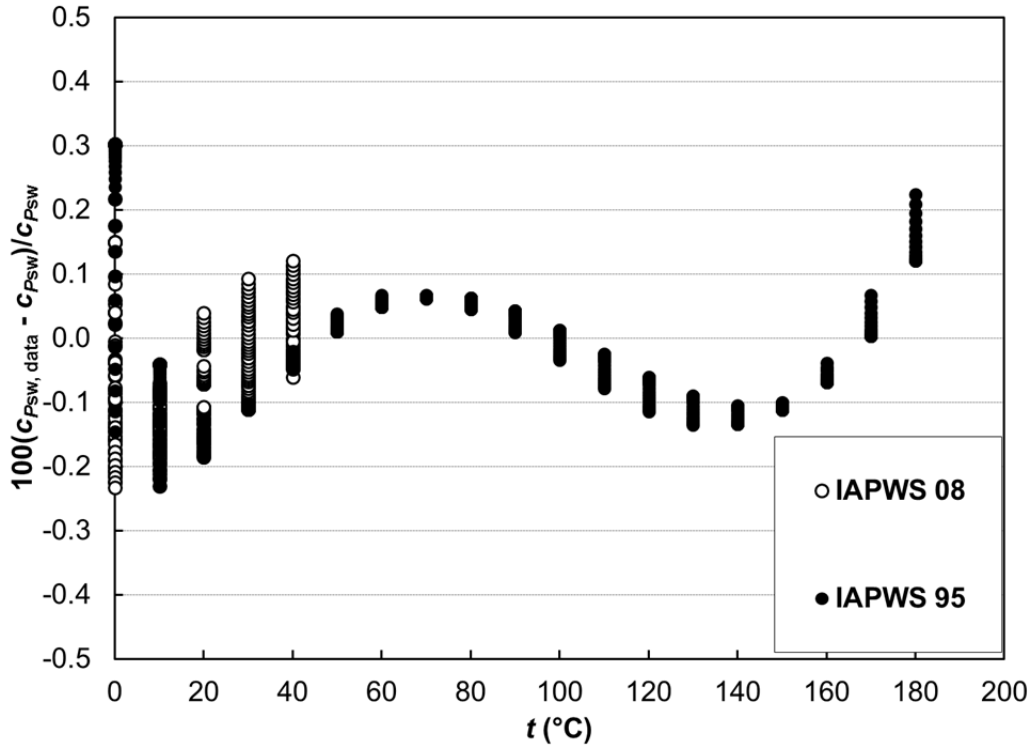|	Range	U_{max}
Literature data	$0 \leq t \leq 180$ °C; $0 \leq S \leq 180$ g/kg; $0.1 \leq P = P_0 \leq 1$ MPa;	±1 %
	$0 \leq t \leq 180$ °C; $S = 0$ g/kg; $0 \leq P \leq 12$ MPa;	
	$0 \leq t \leq 40$ °C; $0 \leq S \leq 42$ g/kg; $0 \leq P \leq 12$ MPa;	
	Ref: [2,3,49]	
Extrapolation	$40 < t \leq 180$ °C; $0 \leq S \leq 42$ g/kg; $0 \leq P \leq 12$ MPa;	±1 %
	$0 \leq t \leq 180$ °C; $42 \leq S \leq 180$ g/kg; $0 \leq P \leq 12$ MPa;	

Figure 10. Deviation of seawater specific heat capacity obtained from the IAPWS-08 seawater formulation [3] and IAPWS-95 pure water formulation [46] from specific heat capacity calculated using Eq. (22) for temperatures 0–180 °C, for salinities 0–42 g/kg and pressures 0–12 MPa.

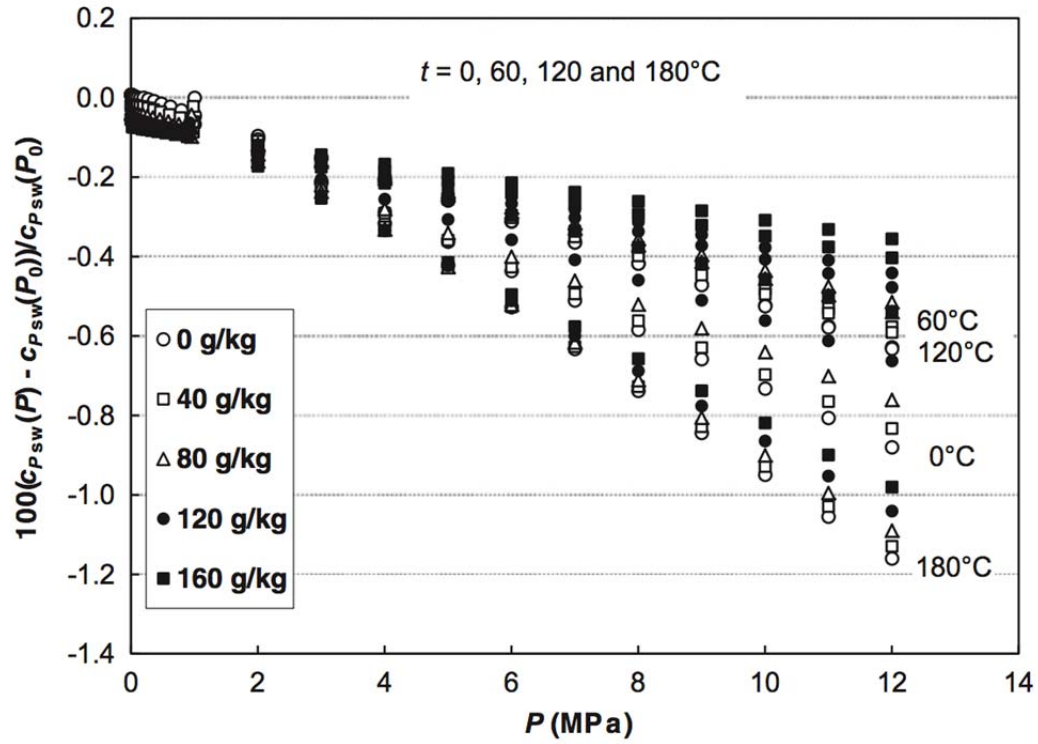Figure 11. Variation of specific heat capacity of seawater with pressure calculated using Eq. (22) normalized with Eq. (23) for salinities S = 0, 40, 80, 120 and 160 g/kg at temperatures t = 0, 60, 120 and 180 °C.

8. Enthalpy

A review of past studies conducted on the enthalpy of seawater was reported by Sharqawy et al. [2] in 2010. The studies were restricted to near atmospheric pressures. Sharqawy et al. also

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proposed a new correlation for the enthalpy of seawater, for temperatures 0–120 °C, for salinities 0–120 g/kg and at pressure P_0. The correlation is given here in Eq. (26). Sharqawy et al. calculated the enthalpy of seawater by adding the saline part of the IAPWS-08 Gibbs function to the pure water enthalpy calculated from the IAPWS-95 function. It must be noted that for temperatures 80–120ºC, the saline part of the Gibbs function was extrapolated beyond its range of validity. To quantify any error that could arise from this extrapolation, enthalpy calculated from Sharqawy's 2010 correlation was compared to enthalpy calculated using the thermodynamic relationship:

$$h_{sw,\,thermo}\left(t,S,P_0\right) = h_{sw,\,sharq}\left(25\,°C, S, 0.101\,MPa\right) + \int_{25}^{t} c_{P,sw}(t,S,P_0)dt + \int_{0.101}^{P_0} \left(\frac{1}{\rho_{sw}} - \frac{(t+273.15)\beta_{P,sw}}{\rho_{sw}} \right) dP$$

(24)

where specific heat capacity $c_{P,\,sw}$ is calculated from Eq. (22), isobaric expansivity $\beta_{P,sw}$ is calculated from Eq. (21) and density ρ_{sw} is calculated from Eq. (18). For an effective comparison the reference value of enthalpy selected was seawater enthalpy at 25 °C and 0.101 MPa calculated from Sharqawy et al.'s 2010 correlation. The percentage deviation between the thermodynamic relationship and the 2010 enthalpy correlation is shown in Fig. 12. It can be seen that Sharqawy's correlation is consistent with the thermodynamic relationship until a temperature of 100 °C after which deviations increase to 1.4 %. This is slightly more than the uncertainty of 1 % in the specific heat capacity of seawater. Thus, the revised uncertainty of Sharqawy's correlation for the temperature range, 100–120 °C, was 1.4 %.
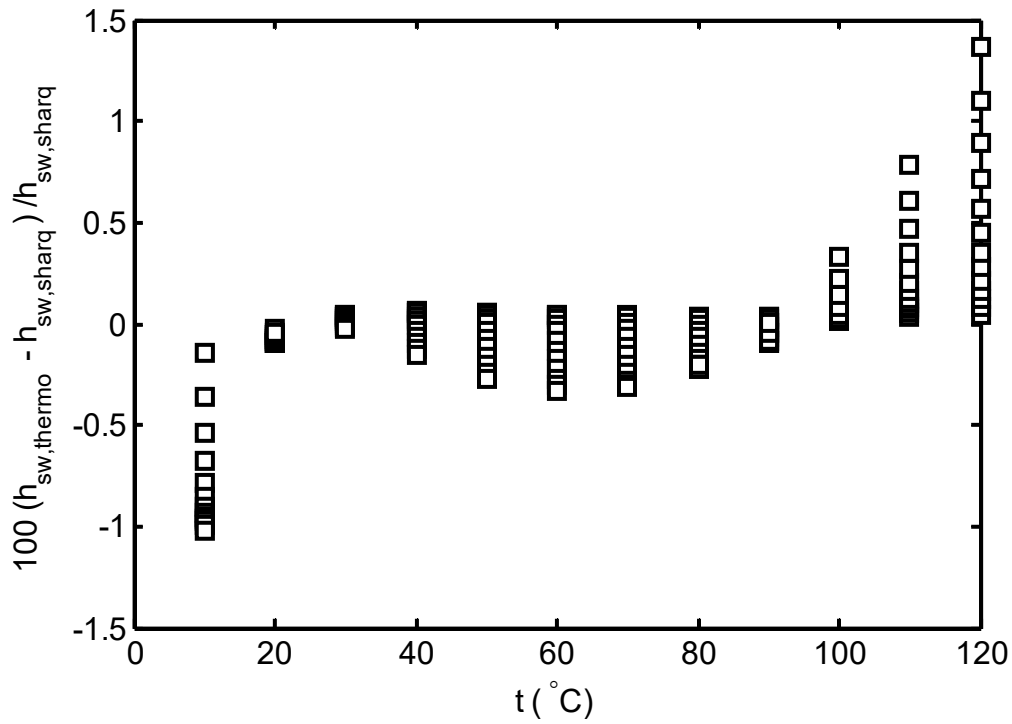
Figure 12. Percentage deviation of seawater enthalpy calculated using the thermodynamic relationship, given in Eq.(24), from Sharqawy et al.'s 2010 correlation for seawater enthalpy [2], given in Eq. (26).

For evaluating enthalpy at high pressures ($0.2 \leq P \leq 12$ MPa), the thermodynamic relationship given in Eq. (13), the enthalpy at pressure P_0 from Sharqawy et al., given in Eq. (26) , and the density relationship seawater density correlation, given in Eq. (18), were used. The evaluated seawater enthalpy at elevated pressures was then correlated to obtain a final expression for the enthalpy of seawater given in Eq. (25). The equation is valid for temperatures 10–120 °C, for salinities 0–120 g/kg and for pressures 0–12 MPa.

For validating the final expression at high pressures in the region of literature data, enthalpy calculated using Eq. (25) was compared with, enthalpy calculated from the IAPWS-08 equation of state for seawater (valid for $0 \leq t \leq 40$ °C, $0 \leq S \leq 42$ g/kg and $0 \leq P \leq 100$ MPa) and, with enthalpy calculated from the IAPWS-95 equation of state for pure water (valid in the liquid

region for $0 \leq t \leq 374$ °C and $0 \leq P \leq 100$ MPa). The percentage deviation between data and the correlation is shown in Fig. 13. The maximum deviation was 0.47 %. This is however lower than the maximum deviation of 1.2 % seen in the earlier comparison with the thermodynamic expression. Thus, 1.2 % was considered as the uncertainty of the correlation in the region of literature data. For the extrapolated region ($10 \leq t \leq 120$ °C; $42 \leq S \leq 120$ g/kg; $0 \leq P \leq 12$ MPa), the error in the enthalpy correlation was estimated by propagating the error in isobaric expansivity and the error in specific heat capacity. The analysis showed a possible maximum deviation of 1.47 %, which was considered as the uncertainty of Eq. (25) in the extrapolated region. A summary of the correlation and its maximum uncertainty is given in Table 9.

To quantify the effect of pressure on the enthalpy of seawater, the percentage deviation in enthalpy due to pressure was evaluated by taking the difference between the enthalpy of seawater at any pressure P, given in Eq. (25), and the enthalpy of seawater at pressure P_0, given in Eq. (26), and normalizing it with the enthalpy at pressure P_0. The evaluated percentage deviation in enthalpy due to pressure at different temperatures and salinities is depicted in Fig. 14. The relative effect of pressure on enthalpy was heavily dependent on the temperature, as the absolute value of enthalpy decreased with temperatures. The maximum increase in enthalpy with pressure was 31.3 %, observed at 12 MPa for seawater of salinity 120 g/kg at 10 °C. The corresponding value at 120 °C with other parameters held constant was only 1.9 %. Overall, the effect of pressure on seawater enthalpy was not negligible when compared with the maximum uncertainty of the correlation.
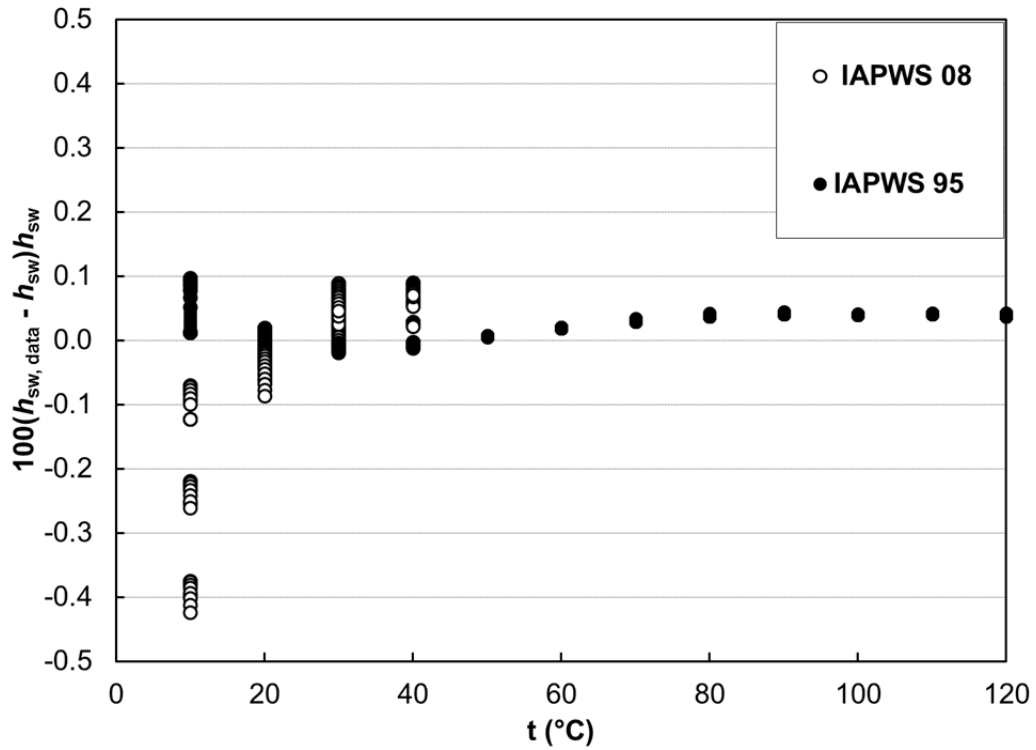
45

Figure 13. Deviation of seawater enthalpy obtained from the IAPWS-08 seawater formulation [3] and IAPWS-95 pure water formulation [46] from specific heat capacity calculated using Eq. (25) for temperatures 0–180 °C, for salinities 0–42 g/kg and pressures 0–12 MPa.
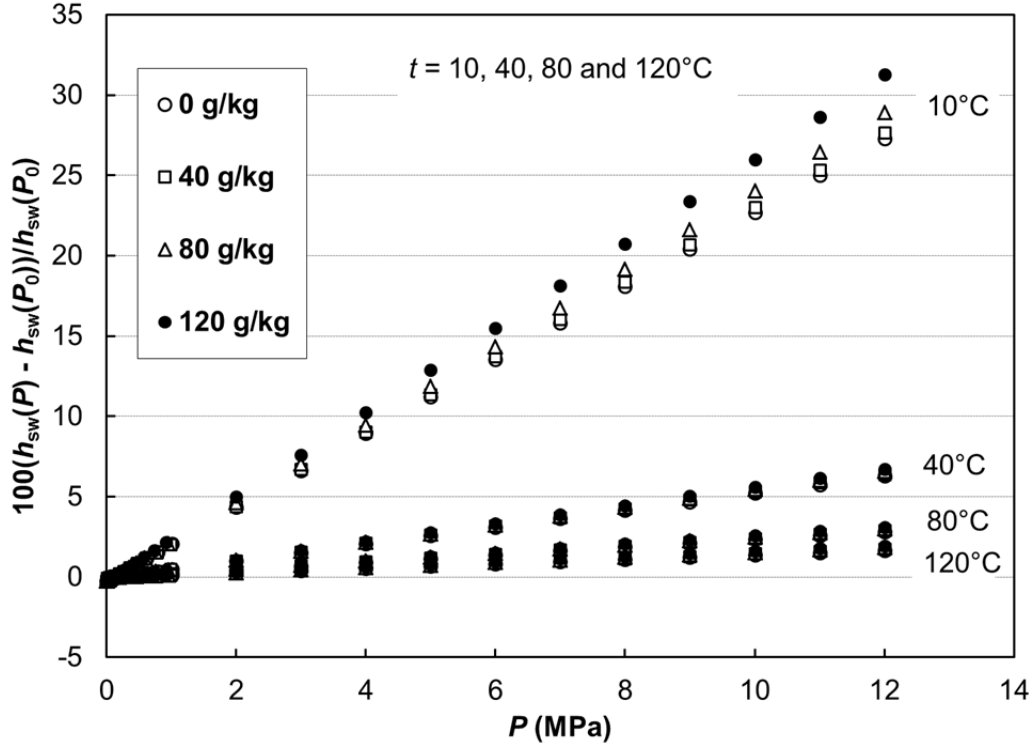
Figure 14. Variation of specific enthalpy of seawater with pressure calculated using Eq. (25) normalized with Eq. (26) for salinities $S = 0$, 40, 80 and 120 g/kg at temperatures $t = 10$, 40, 80 and 120 °C.

Table 9. Seawater specific enthalpy.

Equations:

h_{sw} in J/kg, t in °C, S in g/kg and P in MPa;

$$h_{sw}(t,S,P) = h_{sw}(t,S,P_0) + (P - P_0) \times (a_1 + a_2 t + a_3 t^2 + a_4 t^3 + S \times (a_5 + a_6 t + a_7 t^2 + a_8 t^3)) \quad (25)$$

where

$$h_{sw}(t,S,P_0) = h_w(t) - S_{kg/kg} \times \begin{pmatrix} b_1 + b_2 S_{kg/kg} + b_3 S_{kg/kg}^2 + b_4 S_{kg/kg}^3 + b_5 t + b_6 t^2 + b_7 t^3 \\ + b_8 S_{kg/kg} t + b_9 S_{kg/kg}^2 t + b_{10} S_{kg/kg} t^2 \end{pmatrix} \quad (26)$$

$$S_{kg/kg} = \frac{S}{1000}$$

$$a_1 = 996.7767, a_2 = -3.2406, a_3 = 0.0127, a_4 = -4.7723 \times 10^{-5},$$
$$a_5 = -1.1748, a_6 = 0.01169, a_7 = -2.6185 \times 10^{-5}, a_8 = 7.0661 \times 10^{-8}$$

$$b_1 = -2.34825 \times 10^4, b_2 = 3.15183 \times 10^5, b_3 = 2.80269 \times 10^6, b_4 = -1.44606 \times 10^7$$
$$b_5 = 7.82607 \times 10^3, b_6 = -4.41733 \times 10^1, b_7 = 2.1394 \times 10^{-1}, b_8 = -1.99108 \times 10^4$$
$$b_9 = 2.77846 \times 10^4, b_{10} = 9.72801 \times 10^1$$

$$h_w = 141.355 + 4202.07 \times t - 0.535 \times t^2 + 0.004 \times t^3 \tag{27}$$

Range of validity and maximum uncertainty:

	Range	U_{max}
Literature data	$10 \leq t \leq 120$ °C; $S = 0$ g/kg; $0 \leq P \leq 12$ MPa;	
	$10 \leq t \leq 80$ °C; $0 < S \leq 120$ g/kg; $P = 0.1$ MPa;	±1.36 %
	$10 \leq t \leq 40$ °C; $0 \leq S \leq 42$ g/kg; $0 \leq P \leq 12$ MPa;	
	Ref: [3,46,49]	
Extrapolation	$80 \leq t \leq 120$ °C; $0 \leq S \leq 120$ g/kg; ; $0.1 \leq P = P_0 \leq 1$ MPa; $40 \leq t \leq 120$ °C; $0 \leq S \leq 42$ g/kg; $0 \leq P \leq 12$ MPa;	±1.47 %
	$10 \leq t \leq 120$ °C; $42 < S \leq 120$ g/kg; $0 \leq P \leq 12$ MPa	

9. Entropy

A review of past studies conducted on the entropy of seawater was reported by Sharqawy et al. [2] in 2010. The studies were restricted to near atmospheric pressures. Sharqawy et al. also proposed a new correlation for entropy of seawater, for temperatures 0–120 ºC, for salinities 0–120 g/kg and at pressure P_0. The correlation is given here in Eq. (30). Like Sharqawy et al.'s

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enthalpy correlation, the entropy correlation was calculated by adding the saline part of the IAPWS-08 Gibbs function to the pure water entropy calculated from the IAWPWS-95 function. Like the enthalpy correlation, Sharqawy et al. obtained seawater entropy for temperatures 80–120ºC, by extrapolating the saline part of the Gibbs function. To quantify any error that could arise from this extrapolation, entropy calculated from the Sharqawy's 2010 correlation was compared to entropy calculated using the thermodynamic relationship:

$$s_{\text{sw, thermo}}\left(t,S,P_0\right) = s_{\text{sw, sharq}}\left(25\,°\text{C},S,0.101\,\text{MPa}\right) + \int_{25}^{t} \frac{c_P(t,S,P_0)}{t+273.15}\,dt + \int_{0.101}^{P_0} -\frac{\beta_{P,\text{sw}}}{\rho_{\text{sw}}}\,dP \quad (28)$$

where specific heat capacity, $c_{P,\text{sw}}$, is calculated from Eq. (22), isobaric expansivity $\beta_{P,\text{sw}}$ is calculated from Eq. (21), and density ρ_{sw} is calculated from Eq. (18). For an effective comparison the reference value of entropy selected was seawater entropy at 25 °C and 0.101 MPa calculated from Sharqawy et al.'s 2010 correlation. The percentage deviation between the thermodynamic relationship and the 2010 entropy correlation is shown in Fig. 15. It can be seen that Sharqawy's correlation is consistent with the thermodynamic relationship until a temperature of 100 °C after which deviations increase to 1.2 %. This is slightly more than the uncertainty of 1 % in the specific heat capacity of seawater. Thus, the revised maximum uncertainty of Sharqawy's correlation for the temperature range 100–120 °C was 1.2 %.
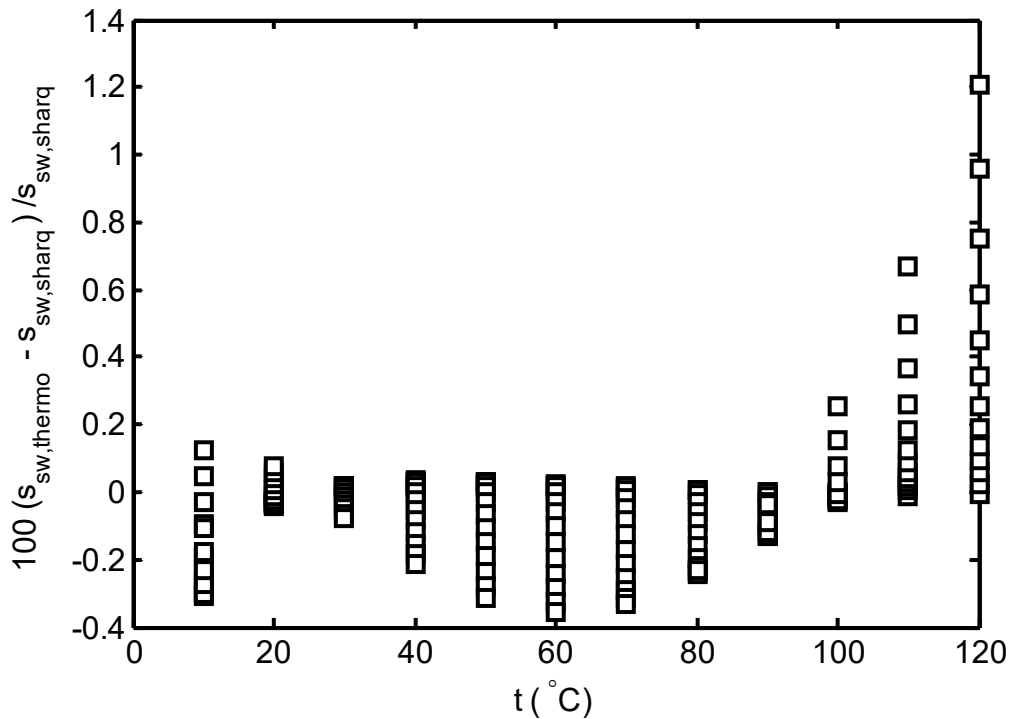
49

Figure 15. Percentage deviation of seawater entropy calculated using the thermodynamic relationship, given in Eq. (28), from Sharqawy et al.'s 2010 correlation for seawater entropy [2], given in Eq. (30).

For evaluating entropy at high pressures ($0.2 \leq P \leq 12$ MPa), the thermodynamic relationship given in Eq.(15), the entropy at pressure P_0 from Sharqawy et al. [2], given in Eq. (30), and the density relationship seawater density correlation, given in Eq. (18), were used. The evaluated seawater entropy at elevated pressures was then correlated to obtain a final expression for the entropy of seawater given in Eq. (29) in Table 10. The equation is valid for temperatures 10–120 °C, for salinities 0–120 g/kg and for pressures 0–12 MPa.

For validating the final expression at high pressures in the region of literature data, entropy calculated using Eq. (29) was compared with, entropy calculated from the IAPWS-08 equation of state for seawater (valid for $0 \leq t \leq 40$ °C, $0 \leq S \leq 42$ g/kg and $0 \leq P \leq 100$ MPa) and, with entropy calculated from the IAPWS-95 equation of state for pure water (valid in the liquid region

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for $0 \leq t \leq 374$ °C and $0 \leq P \leq 100$ MPa). The percentage deviation between data and the correlation is shown in Fig. 16. The maximum deviation was 0.47 %. This was however lower than the maximum deviation of 1.2 % seen in the earlier comparison with the thermodynamic expression. Thus, 1.2 % was considered as the maximum uncertainty of the correlation in the region of literature data. For the extrapolated region ($10 \leq t \leq 120$ °C; $42 \leq S \leq 120$ g/kg; $0 \leq P \leq 12$ MPa), the error in the entropy correlation was estimated by propagating the error in isobaric expansivity and the error in specific heat capacity. The analysis showed a possible maximum deviation of 1.47 %, which was considered as the maximum uncertainty of Eq. (29) in the extrapolated region.

To quantify the effect of pressure on the entropy of seawater, the percentage deviation in entropy due to pressure was evaluated by taking the difference between the entropy of seawater at any pressure P, given in Eq. (29), and the entropy of seawater at pressure P_0, given in Eq. (30), and normalizing it with the entropy at pressure P_0. The evaluated percentage deviation in entropy due to pressure at different temperatures and salinities is depicted in Fig. 17. Entropy reduced by a maximum of 4 % at 12 MPa for seawater of salinity 120 g/kg at 10 °C. The relative effect of pressure on entropy was found to increase with salinity as the absolute value of entropy decreased. Overall, the effect of pressure on seawater entropy was small and was comparable to the maximum uncertainty of the correlation itself.

Table 10. Seawater specific entropy.

Equations:

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s_{sw} in J/kg-K, t in °C, S in g/kg and P in MPa;

$$s_{sw}(t,S,P) = s_{sw}(t,S,P_0) + (P-P_0) \times (a_1 + a_2 t + a_3 t^2 + a_4 t^3 + S \times (a_5 + a_6 t + a_7 t^2 + a_8 t^3)) \quad (29)$$

where,

$$s_{sw}(t,S,P_0) = s_w(t) - S_{kg/kg} \begin{pmatrix} b_1 + b_2 S_{kg/kg} + b_3 S_{kg/kg}{}^2 + b_4 S_{kg/kg}{}^3 + b_5 t + b_6 t^2 + b_7 t^3 + \\ b_8 S_{kg/kg} t + b_9 S_{kg/kg}{}^2 t + b_{10} S_{kg/kg} t^2 \end{pmatrix} \quad (30)$$

where,

$S_{kg/kg} = S/1000$

$$s_w = 0.1543 + 15.383 \times t - 2.996 \times 10^{-2} \times t^2 + 8.193 \times 10^{-5} \times t^3 - 1.370 \times 10^{-7} \times t^4 \quad (30)$$

$a_1 = -4.4786 \times 10^{-3}, a_2 = -1.1654 \times 10^{-2}, a_3 = 6.1154 \times 10^{-5}, a_4 = -2.0696 \times 10^{-7},$
$a_5 = -1.5531 \times 10^{-3}, a_6 = 4.0054 \times 10^{-5}, a_7 = -1.4193 \times 10^{-7}, a_8 = 3.3142 \times 10^{-10}$

$b_1 = -4.231 \times 10^2, b_2 = 1.463 \times 10^4, b_3 = -9.880 \times 10^4, b_4 = 3.095 \times 10^5, b_5 = 2.562 \times 10^1$
$b_6 = -1.443 \times 10^{-1}, b_7 = 5.879 \times 10^{-4}, b_8 = -6.111 \times 10^1, b_9 = 8.041 \times 10^1, b_{10} = 3.035 \times 10^{-1}$

Range of validity and maximum uncertainty:

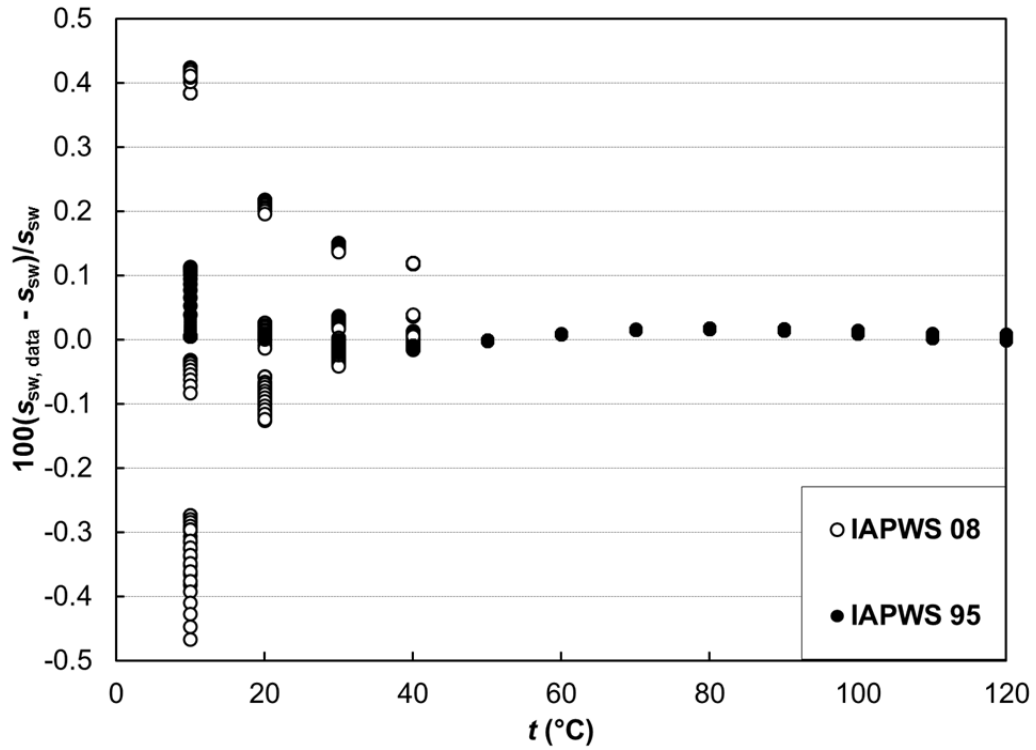|	Range	U_{max}
Literature data	$10 \le t \le 120$ °C; $S = 0$ g/kg; $0 \le P \le 12$ MPa;	
	$10 \le t \le 80$ °C; $0 < S \le 120$ g/kg; $P = 0.1$ MPa;	±0.50 %
	$10 \le t \le 40$ °C; $0 \le S \le 42$ g/kg; $0 \le P \le 12$ MPa;	
	Ref: [3,46,49]	
Extrapolation	$80 \le t \le 120$ °C; $0 \le S \le 120$ g/kg; $0.1 \le P = P_0 \le 1$ MPa;	
	$40 \le t \le 120$ °C; $0 \le S \le 42$ g/kg; $0 \le P \le 12$ MPa;	±1.47 %
	$10 \le t \le 120$ °C; $42 < S \le 120$ g/kg; $0 \le P \le 12$ MPa;	

Figure 16. Deviation of seawater entropy data from the IAPWS-08 seawater formulation [3] and IAPWS-95 pure water formulation [46] from entropy calculated using Eq. (29) for temperatures 0–180 °C, for salinities 0–42 g/kg and pressures 0–12 MPa.
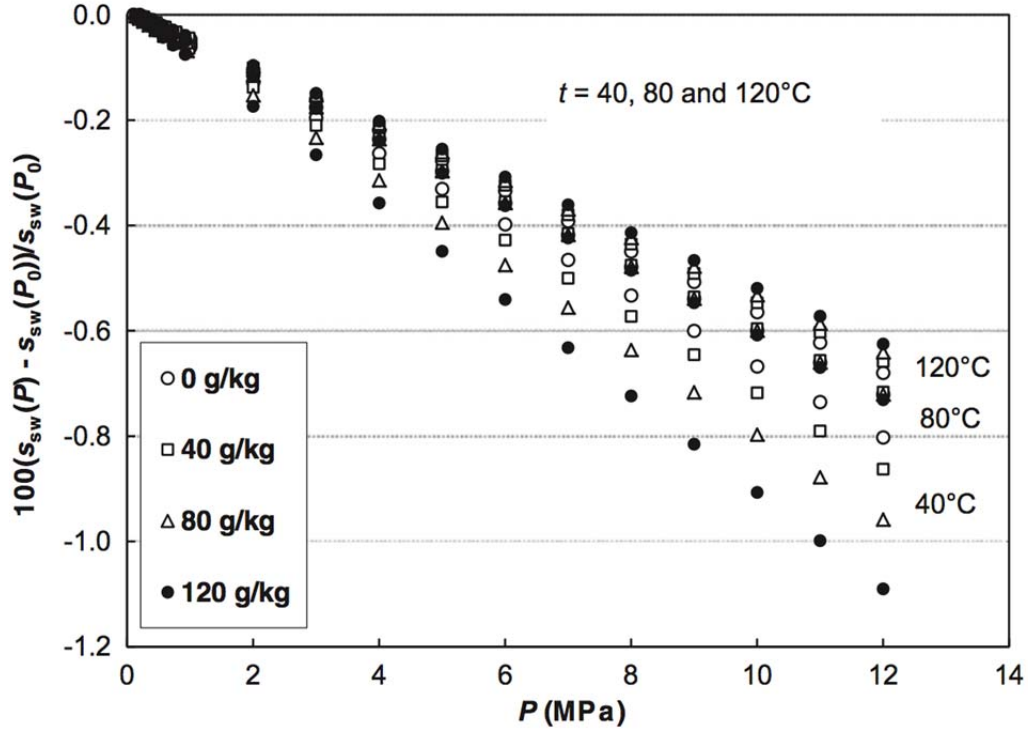
Figure 17. Variation of entropy of seawater with pressure calculated using Eq. (29) normalized with Eq. (30) for salinities $S = 0$, 40, 80 and 120 g/kg at temperatures $t = 40$, 80 and 120 °C.

10. Gibbs energy

10.1 Need for a new correlation

Gibbs energy of seawater can be expressed as a thermodynamic function of the enthalpy and entropy of seawater as:

$$g_{sw} = h_{sw} - Ts_{sw} \tag{31}$$

However, when using such a formulation for Gibbs energy, one needs to be cognizant of error propagation and error in the derivatives resulting from the accuracy limitations of the

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correlations for enthalpy and entropy of seawater. This can be best understood by analyzing

Gibbs energy of seawater calculated using correlations for the enthalpy and entropy of seawater,

originally proposed in 2010 by some of the authors of this work [2]:

$$g_{sw,\,10} = h_{sw,\,10} - T s_{sw,10} \tag{32}$$

where, $h_{sw,\,10}$ and $s_{sw,10}$ correspond to Eqs. (26) and (30)in this paper. Since, $h_{sw,\,10}$ and $s_{sw,10}$ were

both correlated using data from the IAPWS-08 seawater formulation, for an accurate

comparison, $g_{sw,\,10}$ was also compared with Gibbs energy calculated from the IAPWS-08

function ($g_{sw,\,08}$). The percentage deviation and the actual deviation between these were

calculated for temperatures 0-120 °C and for salinities 0-120 g/kg at pressure P_0 are shown in

Fig. 18 (a) and (b). The MAPD was 66.6 % while the MAD was 0.36 kJ/kg. The percentage

deviations in Gibbs energy were high in part because Gibbs energy approaches 0 kJ/kg at certain

temperatures and salinities (e.g., at $t = 40$ °C and $S = 110$ g/kg). In general, percentage deviations

are not a reliable way of estimating correlation maximum uncertainty when the value of the

correlated quantity approaches zero. Hence, for Gibbs energy of seawater, what is more

important is the deviation between the correlation and the actual value. To understand whether

the actual deviations were small enough or not, a comparison was made with the value for the

minimum least work for desalination of seawater, an important thermodynamic calculation based

on the Gibbs energy of seawater. While the MAD was 0.36 kJ/kg, the minimum least work for

desalination of seawater is only 2.71 kJ/kg [50]. Clearly, the deviation in Gibbs energy is not

small enough for engineering applications.

(a)   **(b)**

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Figure 18. (a) Percentage deviation and (b) deviation of Gibbs energy of seawater data from the IAPWS-08 seawater formulation [3] from Gibbs energy calculated using the 2010 formulation, denoted by Eq. (32), for temperatures 0–120 °C, for salinities 0–120 g/kg at pressure P_0.

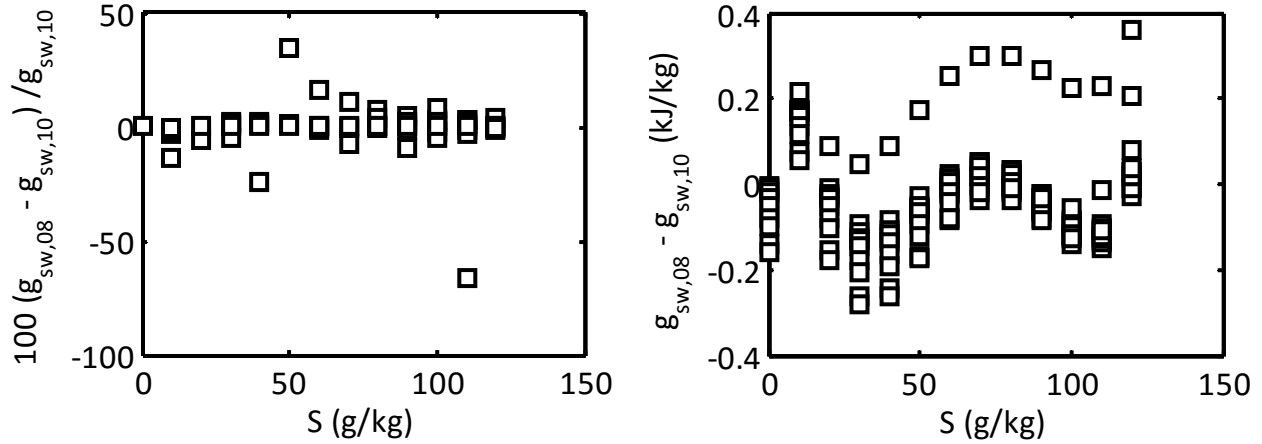The reason for the high deviations is that, inherent in the formulation given in Eq. (32) is the problem of error propagation, error magnification and also error in the derivatives. While $h_{sw,10}$ and $Ts_{sw,10}$ can be large values depending on the temperature, their difference in comparison, is much smaller in magnitude, increasing the relative error. Also, the absolute temperature has a multiplying effect on the error in entropy contributing to an uncertainty in Gibbs energy much higher than the 1 % uncertainty in the constituent $h_{sw,10}$ and $s_{sw,10}$. Furthermore, the polynomials for $h_{sw,10}$ and $s_{sw,10}$ do not capture the derivatives of $g_{sw,10}$ accurately. A new more accurate correlation for Gibbs energy of seawater is thus needed for engineering calculations.

10.2 Obtaining a new correlation at P_0

To reduce the error in the Gibbs energy of seawater while not compromising on the accuracy of the formulations for entropy and enthalpy, we decided to make a new correlation for Gibbs energy of seawater. The approach used was similar to that used for correlating seawater enthalpy and entropy; a correlation for Gibbs energy of seawater valid for pressures P_0 was first obtained, after which the pressure dependence was added.

For the seawater Gibbs energy correlation valid at pressures P_0, raw data were obtained for temperatures 0-120 °C and for salinities 0-120 g/kg from the IAPWS-08 seawater formulation. While the IAPWS-08 seawater formulation is not proven to be valid for the temperature range 80-120 °C, raw data for these temperatures were obtained by extrapolating the saline part of the IAPWS-08 formulation [3] and adding it to the pure water properties from the IAPWS-95 formulation [46]. The raw data were used to obtain a best-fit correlation for Gibbs energy of seawater at pressures P_0, given in Eq. (37). To quantify the error of extrapolating Gibbs for temperatures 80-120 °C, the result of the correlation was compared to Gibbs energy obtained from the thermodynamic relationship given by:

$$
\begin{aligned}
g_{sw,\,thermo}\left(t,S,P_0\right) &= h_{sw,\,thermo}\left(t,S,P_0\right) - (t+273.15\ \text{K}) \times s_{sw,\,thermo}\left(t,S,P_0\right) \\
&= g_{sw,\,10}\left(25°\text{C},S,0.101\,\text{MPa}\right) + \int_{25}^{t} c_{P,sw}(t,S,P_0)\partial t - T\int_{25}^{t} \frac{c_{P,sw}(t,S,P_0)}{T}\partial t + \int_{0.101}^{P_0}\left(\frac{1}{\rho_{sw}}\right)\partial P
\end{aligned}
\tag{33}
$$

where specific heat capacity, $c_{P,\,sw,}$ is calculated from Eq. (22) , density, ρ_{sw}, is calculated from Eq.(18), and a reference condition of 25 °C and 0.101 MPa was chosen. The percentage deviations and the actual deviations between the new correlation, the IAPWS-08 and the thermodynamic formulations are shown in Fig. 19 (a) and (b). The deviations were calculated for

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temperatures 0-120 ºC and for salinities 0-120 g/kg at pressure P_0. The deviations were higher from the thermodynamic formulation with the MAPD being 9.0 % and the AAD 0.07 kJ/kg. This corresponds to a 5-fold improvement in accuracy when compared to Gibbs energy calculated using Eq. (31). Here again, the MAPD appears high only because the Gibbs energy of seawater approaches zero at certain temperatures and salinities. The relevant determinant of maximum uncertainty for Gibbs energy of seawater is the absolute deviation. Thus, the maximum uncertainty of the correlation at pressure P_0 was 0.07 kJ/kg.

(a)   **(b)**
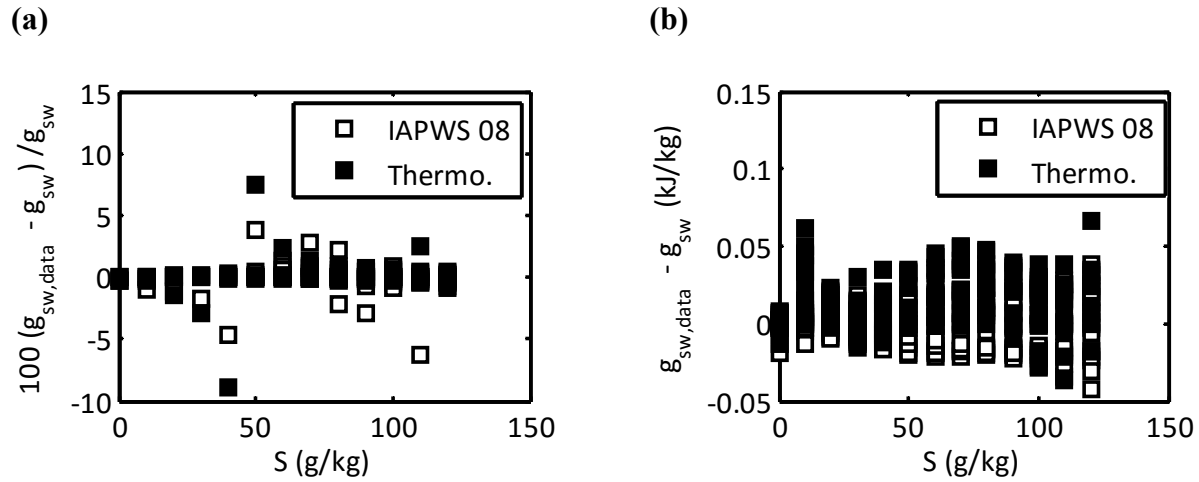
Figure 19. (a) Percentage deviation and (b) deviation of Gibbs energy of seawater data from the IAPWS-08 seawater formulation [3] and the thermodynamic formulation (given in Eq. (33)) from Gibbs energy calculated using Eq. (37) for temperatures 0–120 °C, for salinities 0–120 g/kg at pressure P_0.

10.3 Extending the correlation to $0 \leq P \leq 12$ MPa

For evaluating Gibbs energy of seawater for pressures 0-12 MPa, the thermodynamic relationship given in Eq. (14), the Gibbs energy at pressure P_0 given in Eq. (37), and the density relationship seawater density correlation, given in Eq. (18), were used. The evaluated Gibbs

energy of seawater at elevated pressures was then correlated to obtain a final expression for the Gibbs energy of seawater given in Eq. (36). The equation was valid for temperatures 10–120 °C, for salinities 0–120 g/kg and for pressures 0–12 MPa.

For validating the final expression at high pressures in the region of literature data, Gibbs energy calculated using Eq. (36), was compared with, Gibbs energy calculated from the IAPWS-08 seawater formulation (for $0 \leq t \leq 40$ °C, $0 \leq S \leq 42$ g/kg and $0 \leq P \leq 12$ MPa) and with Gibbs energy calculated from the IAPWS-95 equation of state for pure water (for $0 \leq t \leq 120$ °C and $0 \leq P \leq 12$ MPa). The percentage deviations and the actual deviations between the data and the correlation are shown in Fig. 20 (a) and (b). The deviations were calculated for temperatures 0-120 ºC and for salinities 0-120 g/kg at pressure P_0. The MAPD was 117.41 % at $S = 0$ g/kg, $t = 20$ °C and $P = 3$ MPa, when the Gibbs energy is approximately 0 kJ/kg. The MAD was: 0.03 kJ/kg at $S = 42$ g/kg, $t = 30$ °C and $P = 12$ MPa. Thus, in the region where literature data exists:

$0 \leq t \leq 120$ °C, $0 \leq S \leq 120$ g/kg and $P = P_0$;

$0 \leq t \leq 40$ °C, $0 \leq S \leq 40$ g/kg and $0 \leq P \leq 12$ MPa;

$0 \leq t \leq 120$ °C, $S = 0$ g/kg and $0 \leq P \leq 12$ MPa,

the overall uncertainty of the Gibbs energy correlation was 0.07 kJ/kg.

To assess the maximum uncertainty of the Gibbs energy correlation in the region where data does not exist, the maximum deviation was estimated by propagating the errors in the constituents of the correlation. Equation (36) can be re-written as:

$$g_{sw}\left(t,S,P\right) = g_{sw}\left(t,S,P_0\right) + \int_{P_0}^{P}\left(\frac{1}{\rho_{sw}}\right)dP + \epsilon(g_{sw,correl.}\left(P-P_0\right)) \qquad (34)$$

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where, $\epsilon(g_{sw,correl.}(P - P_0))$ is the deviation between the correlation and the calculated pressure

dependence. The maximum deviation in the correlation can be conservatively estimated as:

$$\epsilon_{max}\left(g_{sw}\left(P\right)\right) = |\epsilon_{max}\left(g_{sw}\left(P_0\right)\right)| + \left|\epsilon_{max}\left(\int_{P_0}^{P}\left(\frac{1}{\rho_{sw}}\right)dP\right)\right| + |\epsilon(g_{sw,correl.}(P - P_0))| \qquad (35)$$

where, $|\epsilon_{max}\left(g_{sw}\left(P_0\right)\right)|$ is the maximum deviation in the correlation at pressures P_0,

$\epsilon_{max}\left(\int_{P_0}^{P}\left(\frac{1}{\rho_{sw}}\right)dP\right)|$ is the maximum uncertainty in the thermodynamic pressure dependence, and

$|\epsilon(g_{sw,correl.}(P - P_0))|$ is the maximum deviation in the correlation capturing the pressure

dependence. Substituting the numerical values for each, we get that,

$\epsilon_{max}\left(g_{sw}\left(P\right)\right) = 0.0662\ \text{kJ/kg} + 0.0262\ \text{kJ/kg} + 0.0165\ \text{kJ/kg} = 0.1089\ \text{kJ/kg} \approx 0.11\ \text{kJ/kg}.$ The

maximum uncertainty of the Eq. (36) in ranges where literature data is unavailable is thus 0.11

kJ/kg. It must be noted here that the estimate is a conservative upper bound; for the most part, the

correlation is expected to be more accurate than 0.11 kJ/kg.

A summary of the correlation for Gibbs energy of seawater, its validity range and its maximum

uncertainty is given in Table 11.

A representation of the variation of the Gibbs energy of seawater is shown in Fig. 21 where

the Gibbs energy of seawater, calculated from Eq. (36), is plotted against pressure for salinities

0-120 g/kg and temperatures 40-120 °C. It can be clearly seen that Gibbs energy of seawater is 0

kJ/kg under certain combinations of temperature, salinity, and pressure. It must be reiterated here

that, at these points, the percentage deviation in the correlation may be very large; but the

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absolute deviations even here are small (< 0.11 kJ/kg). For calculations involving Gibbs energy, more than the absolute value, it is the difference in Gibbs energy that matters; the relevant maximum uncertainty estimate is thus the absolute deviation not the percentage deviation. It is further recommended that for maximum uncertainty estimation in calculations involving Eq. (36) , the uncertainty in the correlation—0.07 kJ/kg or 0.11 kJ/kg depending on the range of interest—be propagated to verify if the uncertainty in the correlation is acceptable for the calculation considered.

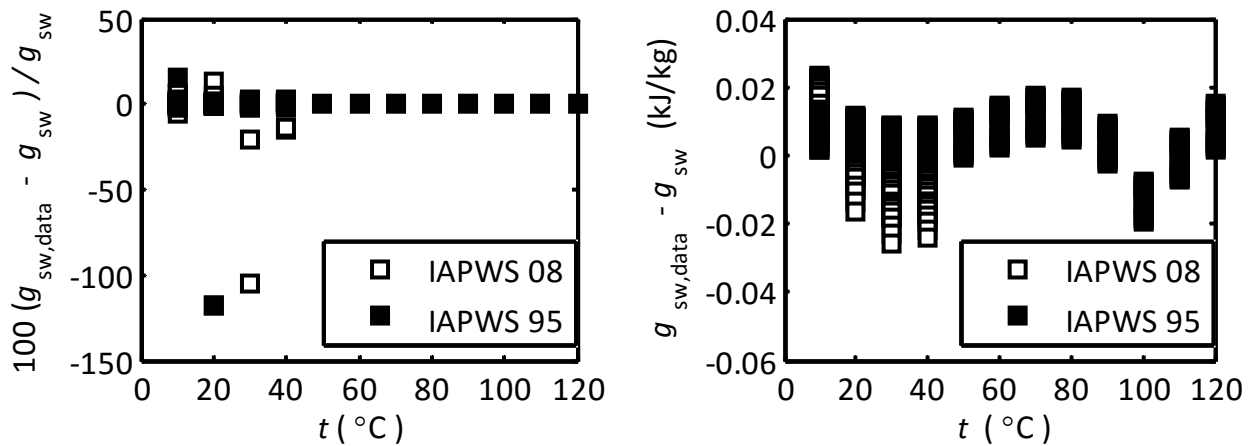Figure 20. (a) Percentage deviation and (b) deviation of Gibbs energy of seawater data from the IAPWS-08 seawater formulation [3] (for $0 \leq t \leq 40$ °C, $0 \leq S \leq 42$ g/kg and $0 \leq P \leq 12$ MPa) and pure water data from the IAPWS-95 formulation (for $0 \leq t \leq 120$ °C and $0 \leq P \leq 12$ MPa) from Gibbs energy calculated using Eq. (36).

Table 11. Seawater Gibbs energy.

Equations:

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g_{sw} in J/kg-K, t in °C, S in g/kg and P in MPa;

$$g_{sw}(t,S,P) = g_{sw}(t,S,P_0) + (P-P_0) \times (a_1 + a_2 t + a_3 t^2 + a_4 t^3 + S \times (a_5 + a_6 t + a_7 t^2 + a_8 t^3)) \quad (36)$$

where,

$$g_{sw}(t,S,P_0) = g_w(t,P_0) + S \times \left[b_1 + b_2 t + b_3 t^2 + b_4 S^2 t + b_5 S^2 t^2 + b_6 S^3 + b_7 S^3 t^2 + b_8 \ln(S) + b_9 \ln(S)t \right]$$
(37)

$$g_w(t,P_0) = c_1 + c_2 t + c_3 t^2 + c_4 t^3 + c_5 t^4 \quad (38)$$

$a_1 = 996.1978, a_2 = 3.4910 \times 10^{-2}, a_3 = 4.7231 \times 10^{-3}, a_4 = -6.9037 \times 10^{-6},$
$a_5 = -7.2431 \times 10^{-1}, a_6 = 1.5712 \times 10^{-3}, a_7 = -1.8919 \times 10^{-5}, a_8 = 2.5939 \times 10^{-8}$

$b_1 = -2.4176 \times 10^2, b_2 = -6.2462 \times 10^{-1}, b_3 = 7.4761 \times 10^{-3}, b_4 = 1.3836 \times 10^{-3},$
$b_5 = -6.7157 \times 10^{-6}, b_6 = 5.1993 \times 10^{-4}, b_7 = 9.9176 \times 10^{-9}, b_8 = 6.6448 \times 10^1,$
$b_9 = 2.0681 \times 10^{-1}$

$c_1 = 1.0677 \times 10^2, c_2 = -1.4303, c_3 = -7.6139, c_4 = 8.3627 \times 10^{-3},$
$c_5 = -7.8754 \times 10^{-6}$

Range of validity and maximum uncertainty:

	Range	U_{max}
Literature data	$10 \le t \le 120$ °C; $S = 0$ g/kg; $0 \le P \le 12$ MPa;	± 0.07 kJ/kg
	$10 \le t \le 120$ °C; $0 < S \le 120$ g/kg; $0.1 \le P = P_0 \le 1$ MPa;	
	$10 \le t \le 40$ °C; $0 \le S \le 42$ g/kg; $0 \le P \le 12$ MPa;	
	Ref: [3,46,49]	
Extrapolation	$40 \le t \le 120$ °C; $0 \le S \le 42$ g/kg; $0 \le P \le 12$ MPa;	± 0.11 kJ/kg
	$10 \le t \le 120$ °C; $42 < S \le 120$ g/kg; $0 \le P \le 12$ MPa;	
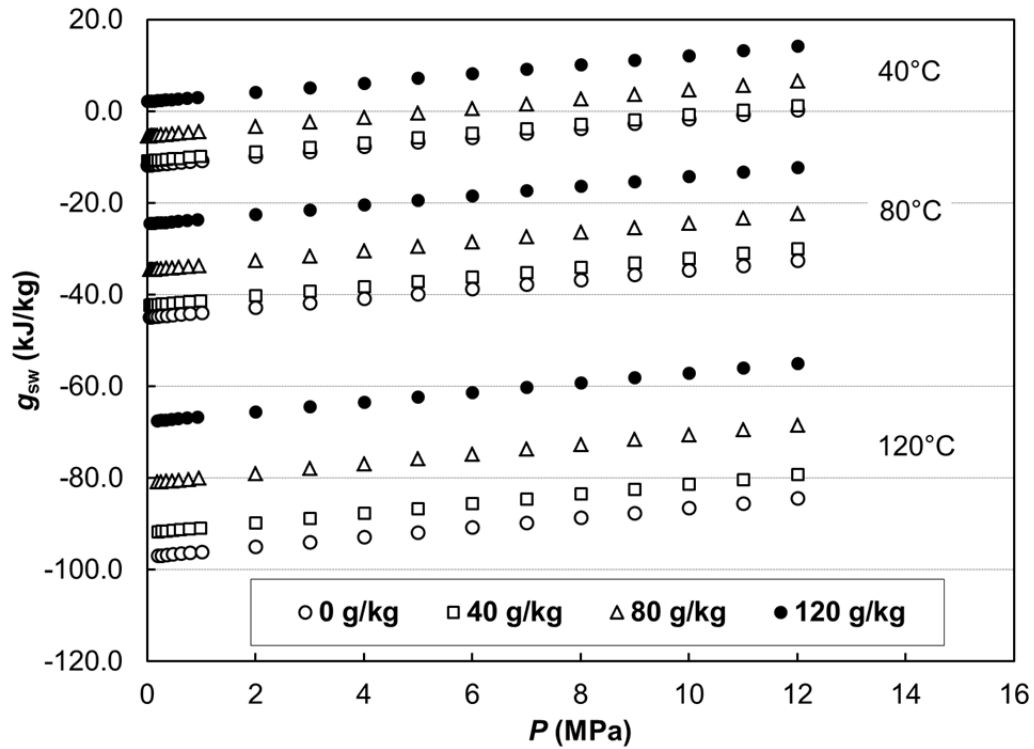
Figure 21. Variation of Gibbs energy of seawater with pressure calculated using Eq. (36) for salinities S = 0, 40, 80 and 120 g/kg at temperatures $t = 40$, 80 and 120 °C.

11. Osmotic coefficient and Osmotic pressure

11.1 Osmotic coefficient

Sharqawy et al. [2] reviewed the literature and found several works which contained osmotic coefficient data for seawater derived from solution vapor pressure, boiling point elevation, or freezing point depression measurements. For developing a correlation, Sharqawy et

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al. chose to correlate the osmotic coefficient data of Bromley et al. [33] due its wide parameter range of 0 – 200 $^{\circ}$C in temperature and 10 – 120 g/kg in salinity with a maximum deviation of ±1.4 % and a correlation coefficient of 0.991.

For many desalination applications, the allowable salinity range in the Bromley data is acceptable. However, with the advent of osmotically driven membrane processes such as pressure retarded osmosis [51], forward osmosis, and assisted forward osmosis, it is possible for a seawater stream to become diluted to a salinity below 10 g/kg, the lowest allowable seawater salinity in the Bromley correlation given in tables. While Bromley gives equations for calculating the osmotic coefficient below 10 g/kg, the expressions are complex. Such complexity is not required for engineering applications given the existence of simpler theoretically-grounded formulations, such as the Brønsted equation for osmotic coefficient [52]. Additionally, the IAPWS-08 equation of state for seawater [3] does calculate osmotic coefficient for salinities below 10 g/kg; however, the original data set used is restricted to greater than 1.7 g/kg, and to temperatures of 0 and 25 °C. Therefore, Sharqawy et al. [51] have extended the Bromley correlation from 0-10 g/kg using Brønsted's equation for temperatures from 0-120 °C. Brønsted's equation [52], which is accurate in the limit of ideal solutions, is:

$$\phi = 1 - \kappa\sqrt{m_s} + \lambda m_s \tag{39}$$

where m_s is the molality (mol/kg) of the solution and κ and λ are two fitting parameters. For the IAPWS seawater composition considered, the molality, m_s, is specified as:

$$m_s = \frac{S}{(1000-S)} \times \frac{1000}{MW_s} \tag{39}$$

where S is salinity in g/kg and MW_s is the weighted average of the molecular weight of each dissolved solute in seawater [14]:

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$$MW_s = 31.4038 \text{ g/mol} \tag{39}$$

To find the fitting parameters κ and λ, we match the value and slope of Eq. (39) (with respect to molality) to the value and slope of the Bromley correlation at 10 g/kg. The constraint that the osmotic coefficient must be unity at 0 g/kg is also used. The fitting parameters κ and λ are a function of the temperature of the seawater solution.

The resultant osmotic coefficient correlation is a piecewise combination of the Brønsted equation for 0-10 g/kg and the Bromley correlation for 10-120 g/kg. The osmotic coefficient for seawater from 0-120 g/kg and 0-120 °C is shown in Fig. 22. Figure 23 shows the deviation of seawater osmotic coefficient calculated from the correlation from values obtained from the IAPWS equation of state for seawater [3].

A summary of the correlation for seawater osmotic coefficient, its validity range and its maximum uncertainty is given in Table 12.
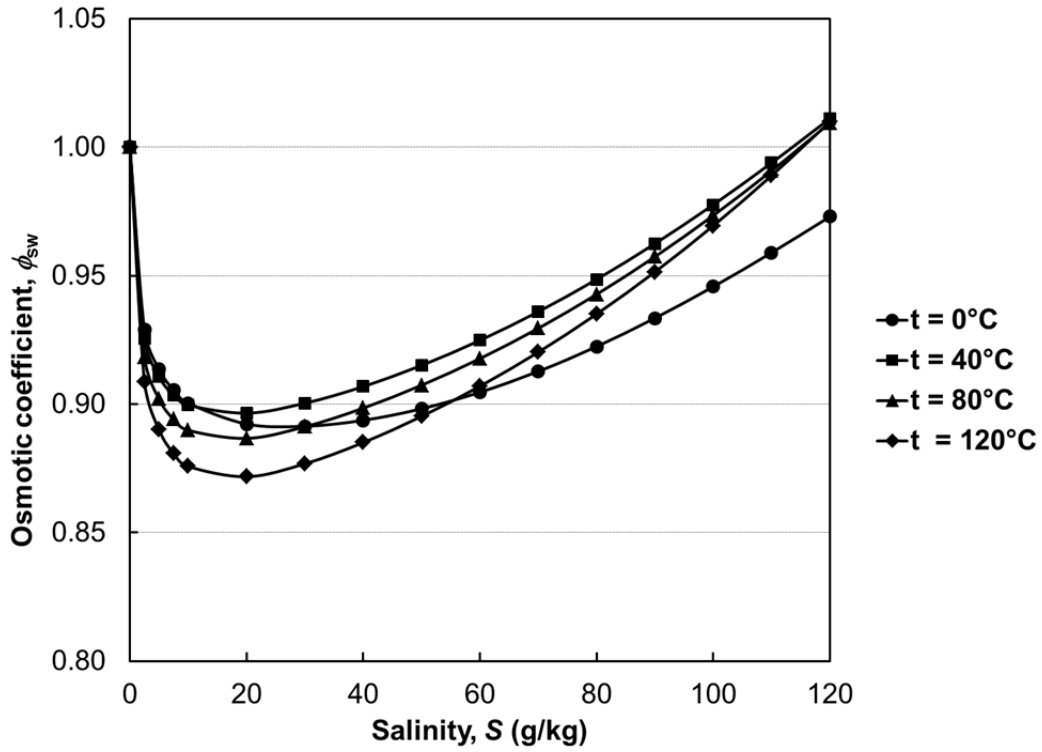
Figure 22. Osmotic coefficient of seawater as a function of salinity and temperature.
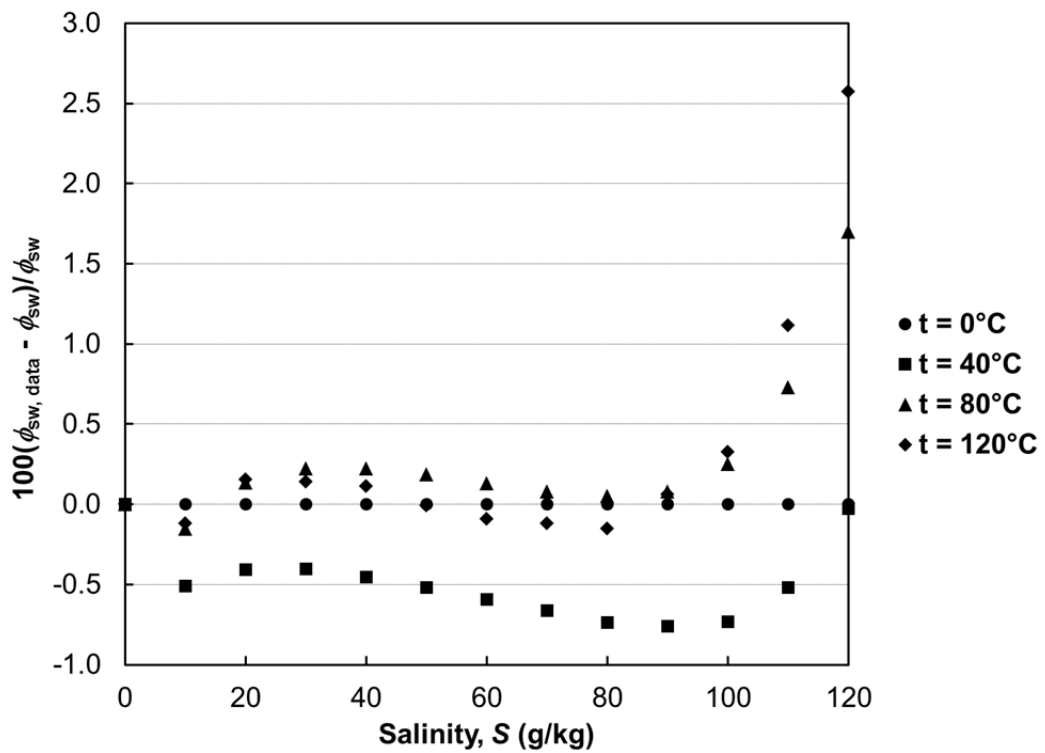
Figure 23. Deviation of osmotic coefficient data calculated using IAPWS-08 from Sharqawy et al.'s correlation updated using the Brønsted's equation.

Table 12. Seawater osmotic coefficient

Equations:

ϕ_{sw} is unit less, t in °C and S in g/kg;

$$\phi_{sw}(t,S) = \begin{cases} \phi_{Bromley}(t,S) \text{ for } S \geq 10 \text{ g/kg} \\ \phi_{Brønsted}(t,S) \text{ for } S < 10 \text{ g/kg} \end{cases}$$

Seawater osmotic coefficient correlation, from Bromley [2]]

$$\phi_{Bromley}(t,S) = a_1 + a_2 t + a_3 t^2 + a_4 t^4 + a_5 S + a_6 St + a_7 St^3 + a_8 S^2 + a_9 S^2 t \qquad (40)$$
$$+ a_{10} S^2 t^2$$

$a_1 = 8.9453233003 \times 10^{-1}; a_2 = 4.1560737424 \times 10^{-4}; a_3 = -4.6262121398 \times 10^{-6};$
$a_4 = 2.2211195897 \times 10^{-11}; a_5 = -1.1445456438 \times 10^{-4}; a_6 = -1.4783462366 \times 10^{-6};$
$a_7 = -1.3526263499 \times 10^{-11}; a_8 = 7.0132355546 \times 10^{-6}; a_9 = 5.6960486681 \times 10^{-8};$
$a_{10} = -2.8624032584 \times 10^{-10}$

Seawater osmotic coefficient for dilute solutions, from Brønsted model[52]:

$$\phi_{Brønsted}(t,S) = 1 - \kappa(t)\sqrt{31.843 \frac{S}{1000-S}} + \lambda(t) \cdot 31.843 \frac{S}{1000-S} \qquad (41)$$

From, equating $\phi_{Brønsted}$ to $\phi_{Bromley}$ and $\left(\frac{\partial \phi_{Brønsted}}{\partial S}\right)$ to $\left(\frac{\partial \phi_{Bromley}}{\partial S}\right)$ at $S = 10$ g/kg, $\kappa(t)$ and

$\lambda(t)$ are:

$$\lambda(t) = 3.1084 \left(1 - \phi_{Bromley}(t)_{S=10\frac{g}{kg}}\right) + 61.5481 \left(\frac{\partial \phi_{Bromley}}{\partial S}\right)_{S=10\frac{g}{kg}} \qquad (42)$$

$$\kappa(t) = 1.7632 \left(1 - \phi_{Bromley}(t)_{S=10\frac{g}{kg}} + 0.3216 \cdot \lambda(t)\right) \qquad (43)$$

Range of validity and maximum uncertainty: ϕ_{sw} in (-);

	Range	U_{max}
Bromley correlation	$0 \leq t \leq 120$ °C; $10 \leq S \leq 120$ g/kg Ref: [3]	±2.57 %
Brønsted model	$0 \leq t \leq 120$ °C; $0 < S \leq 10$ g/kg;	±0.78 %

11.2 Osmotic pressure

From Robinson and Stokes [53], osmotic pressure for any solution can be calculated as a function of osmotic coefficient and other parameters:

$$\pi = \phi(RT\rho_{solvent}) \sum_{j=solutes} m_j \tag{44}$$

where R is 8.3145 J mol^{-1} K^{-1}, the universal gas constant, T is the temperature of the mixture in Kelvin, $\rho_{solvent}$ is solvent density (often pure water is considered), and m_j is the molality of the jth solute in the solution.

For seawater, the osmotic pressure calculation simplifies to:

$$\pi(t,S) = \frac{\phi_{sw} RT \times \rho_{sw}(t, 0 \text{ g/kg}, P_0)}{10^6} \times \frac{S \times 1000}{(1000 - S) \times MW_s} \tag{45}$$

where, $\pi(t,S)$ is the osmotic pressure of seawater in MPa, R is 8.3145 J mol^{-1} K^{-1}, T is the temperature in Kelvin, $\rho_{sw}(t, 0 \text{ g/kg}, P_0)$ is the density of pure water calculated from Eq. (19), MW_s is calculated from Eq. **Error! Reference source not found.** . The uncertainty in osmotic pressure is approximately the same as the uncertainty in the osmotic coefficient described

previously since the uncertainty contributed by the density of pure water is comparatively negligible.

12. Thermal conductivity

A new correlation capturing the pressure dependence of thermal conductivity is presented here. Unlike other properties, experimental data for the thermal conductivity of seawater at elevated pressures is very limited. However, data is available for pure water. Here, we present a simple correlation for the thermal conductivity of pure water. This is then used to extend a correlation for the thermal conductivity of seawater, previously developed by Sharqawy [34], to elevated pressures. Results are validated against results of a theoretical model for the thermal conductivity of seawater reported by Wang and Anderko [54].

Sharqawy [34] developed a correlation for fresh water thermal conductivity valid within a temperature range of 0 °C – 99 °C and a pressure of $P_0 = 0.1$ MPa. His correlation was simpler than the one provided by IAPWS [55] and has a maximum deviation of ±0.06 % from IAPWS [55]. This correlation is given by:

$$k_\mathrm{w} = 0.797015 \times T^{*-0.194} - 0.251242 \times T^{*-4.717} + 0.096437 \times T^{*-6.385} - 0.032696 \times T^{*-2.134} \qquad (46)$$

where k_w is in W/m-K and T^{*} is a dimensionless temperature given by $(t + 273.15)/300$.

A modified version of this equation is developed in this paper to consider the effect of pressure variation. Equation (47) gives the ratio of the thermal conductivity of fresh water at a given pressure and temperature to that one at 0.1 MPa (calculated by Eq. (46)) based on the data given by IAPWS [55].

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$$\frac{k_w(t,P)}{k_w(t,P_o)} = 1 + A \times P^*$$

(47)

where

$$A = 13.464 \times T^{*4} - 60.727 \times T^{*3} + 102.81 \times T^{*2} - 77.387 \times T^* + 21.942$$

(48)

$$P^* = \frac{P - 0.1}{139.9}$$

(49)

The new correlation of fresh water thermal conductivity given by Eq. (47) is valid within a temperature range of 0 – 99 °C and a pressure range of 0.1 – 140 MPa. It has a maximum deviation of 1.1 %, and an average deviation of 0.31 % from IAPWS [55]. Figure 24 shows the deviation between the fresh water thermal conductivity calculated by Eq. (47) and that given by IAPWS [55] within its temperature and pressure validity ranges. Figure 25 shows the variation of the thermal conductivity of fresh water with the pressure and temperature within their validity ranges.
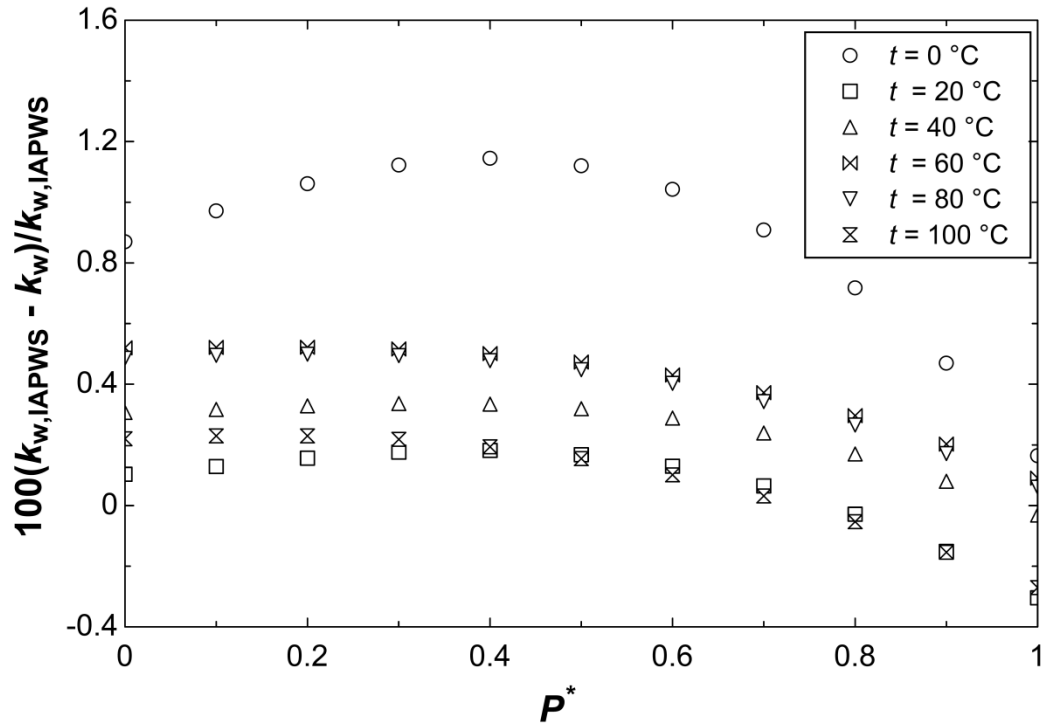
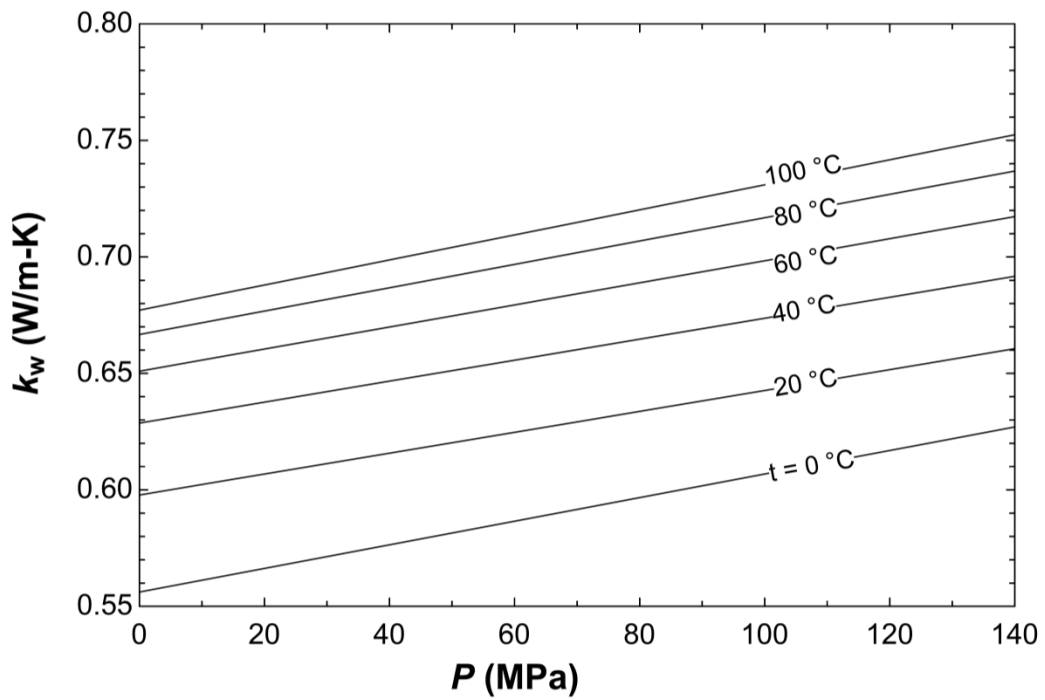Figure 24. Comparison of present work [Eq. (47)] and IAPWS [55] for fresh water thermal conductivity

Figure 25. Fresh water thermal conductivity calculated from Eq. (47)

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Sharqawy [34] developed an empirical correlation (based on his experimental measurements) for the thermal conductivity of seawater given as a ratio of fresh water to seawater (k_w/k_{sw}) thermal conductivities at atmospheric pressure for temperatures 0-90 °C and salinities 0-120 g/kg:

$$\frac{k_w\left(t,P_o\right)}{k_{sw}\left(t,S,P_o\right)}=0.00022\times S+1 \tag{50}$$

where S is the salinity in g/kg. His correlation was independent of the temperature and was verified by both experimental measurements [34] and the theoretical model developed by Wang and Anderko [54]. The correlation, given by Eq. (50), had a maximum deviation of 1 % from the measured values. In addition, different comparisons of the correlation with the available data in literature for seawater thermal conductivity showed a good agreement with the data of Emerson and Jamieson [30] at higher temperatures (40 - 90 °C); an excellent agreement with the data of Fabuss and Korosi [56], and Castelli et al. [57] at a temperature of 10 °C; and an excellent agreement with the data of Tufeu et al. [58], Emerson and Jamieson [30] and Caldwell [59] at a temperature of 30 °C. The uncertainty in Sharqawy's measurements was 2.4 %. Thus, the maximum uncertainty of Eq. (50) was 2.4 %.

To obtain the thermal conductivity of seawater as a function of temperature, salinity and pressure, the correlation for seawater thermal conductivity at atmospheric pressure, given by Eq. (50), was modified to include pressure-dependent thermal conductivity of pure water, given by Eq.(47). The correlation is given by:

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$$\frac{k_w(t,P)}{k_{sw}(t,S,P)} = 0.00022 \times S + 1 \tag{51}$$

To verify, the maximum uncertainty in Eq.(51), the thermal conductivity calculated was compared against data reported by Wang and Anderko [54] for seawater of salinity 35 g/kg for temperatures 0-60 °C and for pressures 0.1-20 MPa. The percentage deviation between the data and the calculated value is shown in Fig. 26. For comparison purposes, also shown is the percentage deviation of the correlation against data on the thermal conductivity of pure water from IAPWS [55]. The MAPD was 2.57 % at $t = 0$ °C and $P = 18.4$ MPa. Thus, the maximum uncertainty of Eq. (51) was 2.57 %.

A summary of the correlation for the thermal conductivity of seawater, its validity range and its maximum uncertainty is given in Table 13.
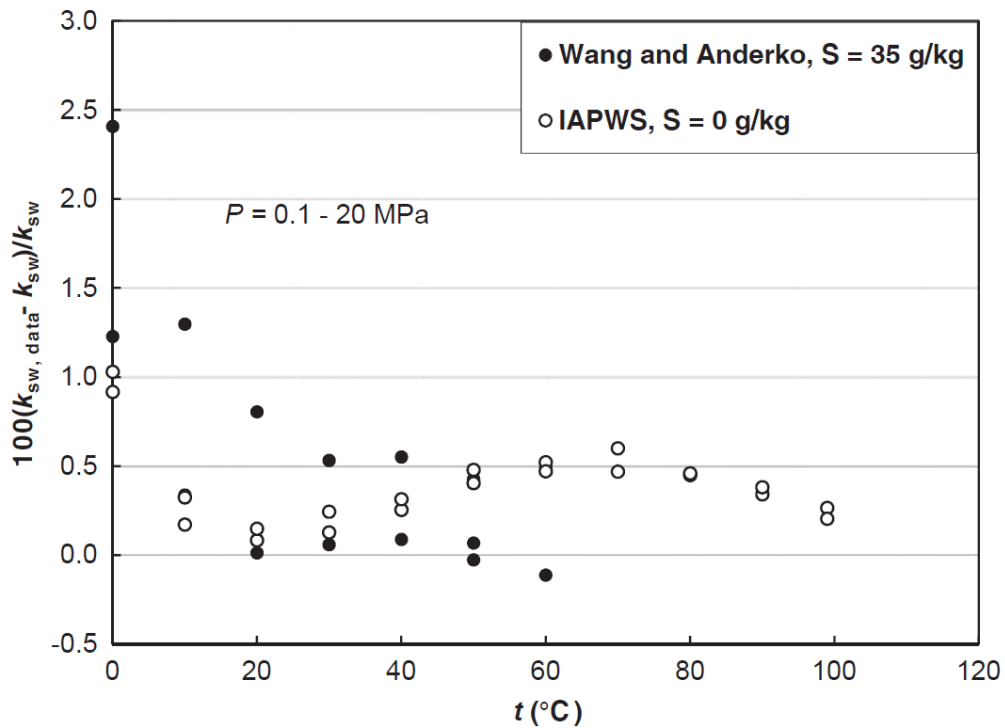
Figure 26. Percentage deviation of thermal conductivity of seawater calculated

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using the relationship, given by Eq. (51), from Wang and Anderko's reported data [33]

for S = 35 g/kg, $0 \leq t \leq 60$ °C and $0.1 \leq P \leq 20$ MPa.

Figure 27 shows the effect of pressure on the thermal conductivity of seawater for temperatures 0-60 °C, for salinities 0-30 g/kg and for pressures 0-12 MPa. Pressure increased the conductivity by 1.1 % at P = 12 MPa when compared with the value at atmospheric pressure. This was, however, smaller than the 2.4 % experimental uncertainty in the data used to generate Eq. (51); thus for thermal conductivity, the effect of pressure can be assumed to be negligible for practical applications.

Figure 27. Variation of the thermal conductivity of seawater with pressure calculated using Eq. (51) normalized with Eq. (50) for salinities S = 0, 10, 20 and 30 g/kg

at temperatures $t = 0, 20, 40$ and $60\,°C$.
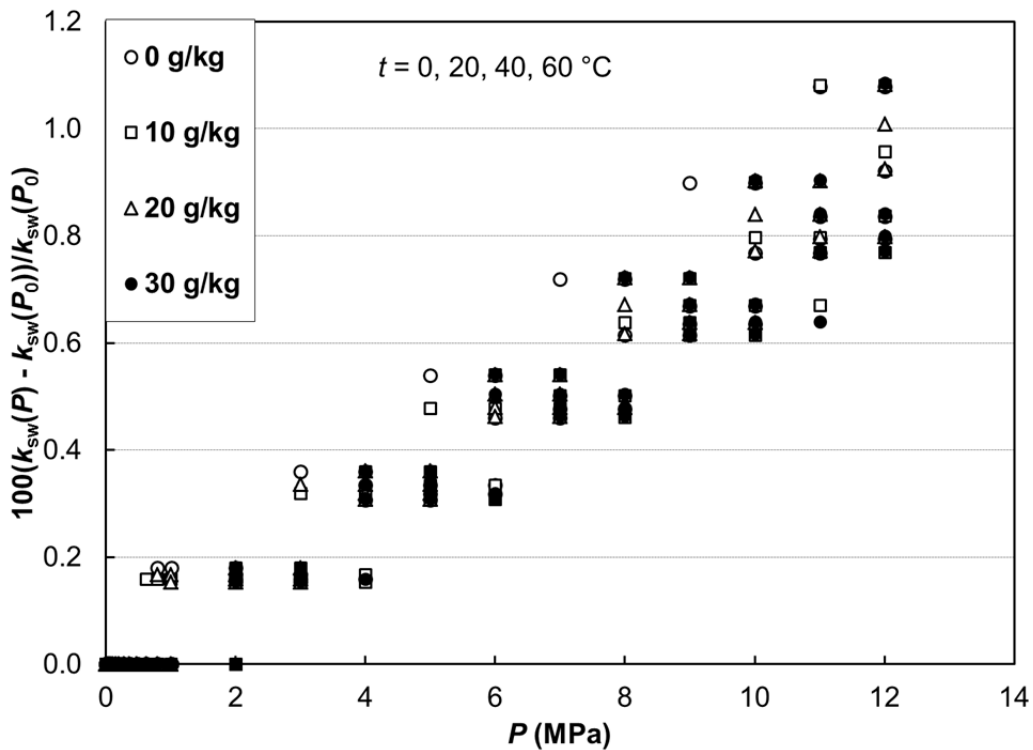
Table 13. Seawater thermal conductivity.

Equations:

k_{sw} in W/m-K, t in °C, S in g/kg and P in MPa;

$$k_{sw}\left(t,S,P\right) = \frac{k_w\left(t,P\right)}{1+0.00022 \times S}$$

$$k_w\left(t,P\right) = k_w\left(t,P_0\right) \times \left[1 + P^* \times (a_1 + a_2 T^* + a_3 T^{*2} + a_4 T^{*3} + a_5 T^{*4})\right]$$

where, $k_w\left(t,P_0\right)$ is from Ref. [34]:

$$k_w(t,P_0) = b_1 T^{*-0.194} + b_2 T^{*-4.717} + b_3 T^{*-6.385} + b_4 T^{*-2.134}$$

$$T^* = \frac{t+273.15}{300};\ P^* = \frac{P-0.1}{139.9}$$

$$a_1 = 21.942, a_2 = -77.387, a_3 = 102.81, a_4 = -60.727, a_5 = 13.464$$

$$b_1 = 0.797015, b_2 = -0.251242, b_3 = 0.096437, b_4 = -0.032696$$

Range of validity and maximum uncertainty: k_{sw} in (W/m-K);

	Range	U_{max}
Literature data	$10 \leq t \leq 90\,°C$; $0 \leq S \leq 120$ g/kg; $P = P_0$;	$\pm 2.57\,\%$
	$10 \leq t \leq 60\,°C$; $0 \leq S \leq 35$ g/kg; $0.1 \leq P \leq 12$ MPa;	
	Ref: [34,54]	

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13. Surface tension

In 2010, Sharqawy et al. developed a correlation for the surface tension of seawater using data reported by Krummel [60] and Chen et al [61]. The correlation was valid for 0-40 °C and 0-40 g/kg and was normalized to the IAPWS correlation for the surface tension of pure water [62] so that at zero salinity both the seawater and pure water correlations matched. Since 2010, two studies have further investigated the surface tension of seawater—Schmidt and Schneider [63] in 2011 and Nayar et al. [64] in 2014. While Schmidt and Schneider presented new results for oceanographic temperature ranges and salinities, Nayar et al. reported what is currently the only available data for surface tension of seawater in the desalination temperature range and salinity. Nayar et al. also critically evaluated existing experimental data for seawater surface tension and developed a reference correlation for the surface tension of seawater. For the benefit of readers, a brief summary of the work done by Schmidt and Schneider and Nayar et al. is presented below.

Schmidt and Schneider had discussed at length how surface active material in natural seawater can reduce its surface tension. Krummel and Chen et al. had not considered this in their experiments. To remove surface active material from seawater, Schmidt and Schneider filtered the seawater and through special surfactant adsorbing cartridges to adsorb the surface active material. Subsequently, surface tension was measured for temperatures 0-40 °C and salinities $S =$ (0, 11, 34) g/kg using the Wihlemy plate method. Schmidt's test procedures were quite rigorous with surface tension measurements for pure water matching to within 0.01 mN/m. However, a detailed uncertainty analysis of Type A and Type B uncertainties was not presented, and the actual data were given only as a correlation based on the data without mentioning the deviation

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of the data from the correlation and the deviations. Schmidt's data could not be accurately determined as they were only presented in a figure.

Nayar et al. reported reference data and a reference correlation for the surface tension of seawater for temperatures 1-92 °C and salinities 0-131 g/kg. The study was the first that measured surface tension of seawater beyond $S = 35$ g/kg and $t = 35$ °C, the oceanographic temperature range and salinity. The Wilhelmy plate method was used to measure surface tension. To avoid the presence of surface active material in their seawater samples, Nayar et al. prepared seawater samples from the ASTM D1141 standard seawater. A detailed uncertainty analysis was conducted for both Type A and Type B uncertainties in the measurements. The average reported expanded uncertainty was 0.22 mN/m while the maximum reported uncertainty was 0.37 mN/m. For developing the reference correlation, Nayar et al. had carefully analyzed the seawater surface tension data of Krummel, Chen et al., Schmidt and Schneider as well as their own measurements for the surface tension of seawater. The final correlation, given by Eq. (52), was reported to be valid for temperatures 1-92 °C and salinities 0-131 g/kg and extrapolatable in temperature to 0-100 °C.

The absolute average deviation between data used to generate the correlation and the correlation itself was 0.19 % while the maximum deviation from the correlation was 0.60 %. The maximum experimental uncertainty reported was 0.57 %; thus the maximum uncertainty of Eq. (52) was 0.60 %. A summary of the correlation for the surface tension of seawater, its validity range and its maximum uncertainty is given in Table 14.

Table 14. Seawater surface tension.

Equations:

γ_{sw} in mN/m, t in °C and S in g/kg;

$$\gamma_{sw} = \gamma_w \left[1 + 3.766 \times 10^{-4}\, S + 2.347 \times 10^{-6}\, S\, t \right] \tag{52}$$

where, γ_w is from Ref. [62] and given by:

$$\gamma_w = 235.8 \left(1 - \frac{t + 273.15}{647.096} \right)^{1.256} \left[1 - 0.625 \left(1 - \frac{t + 273.15}{647.096} \right) \right] \tag{53}$$

Range of validity and maximum uncertainty:

	Range	U_{max}
Literature data	$1 \leq t \leq 92$ °C; $0 \leq S \leq 131$ g/kg; $0.1 \leq P = P_0 \leq 1$ MPa; Ref: [62,64]	±0.60 %
Extrapolation	$1 \leq t \leq 100$ °C; $0 \leq S \leq 131$ g/kg; $0.1 \leq P = P_0 \leq 1$ MPa; Ref: [62,64]	±0.60 %

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14. Concluding Remarks

New correlations are developed that included the effect of pressure on seawater: isothermal compressibility, density, isobaric expansivity, specific heat capacity, enthalpy, entropy and Gibbs energy. These correlations are valid within the desalination range of temperature and salinity up to a pressure of 12 MPa. These property correlations are all valid within the range 10

$\leq t \leq 120\ ^\circ\text{C}$ and $0 \leq S \leq 120$ g/kg. Inaccuracies in deriving Gibbs energy from a previous work [2] were highlighted and a new correlation that increased the accuracy by a factor of 10 was developed in this work. A new correlation was also proposed for seawater vapor pressure. Existing correlations for seawater: surface tension, osmotic coefficient and thermal conductivity were reviewed. A seawater thermal conductivity correlation from the literature was modified to be valid until a pressure of 12 MPa. Maximum uncertainty bounds were obtained for each correlation. These are highlighted in tables corresponding to each correlation. For most properties, the variation across a pressure difference of 12 MPa was around 1 %. For seawater enthalpy, the variation was as high as 31 %. For seawater Gibbs energy, the variation as a percentage was even higher, as the property had a value close to zero at atmospheric pressure for certain temperatures and salinities. A software implementation of the correlations developed in this paper is available at no cost at http://web.mit.edu/seawater.

15. Acknowledgments

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Appendix A: Estimation of uncertainty in isothermal compressibility of seawater and isothermal compressibility of aqueous sodium chloride

A.1 Isothermal compressibility of aqueous sodium chloride

Accurate data for the isothermal compressibility of aqueous sodium chloride has been reported by Rogers and Pitzer [45] for a wide range of temperature, salinities and pressures ($0 \leq t \leq 300$ °C; $0 \leq S \leq 226$ g/kg; $0.1 \leq P \leq 100$ MPa). Since seawater is an electrolyte solution predominantly made up of sodium chloride, inferences on the relationship between isothermal compressibility and salinity made from analyzing the aqueous sodium chloride data of Rogers and Pitzer, could be applied to seawater for predicting property variation. The key inferences presented here deal with how compressibility varies with salinity, whether low salinity compressibility data can accurately predict compressibility at high salinities or not, and whether deviations at low salinity can accurately predict deviations or not.

Analysis of the aqueous sodium chloride data of Rogers and Pitzer, showed that, at constant temperature and pressure, isothermal compressibility has a strong linear relationship with absolute salinity, with the R^2 value between them being consistently above 0.99 for temperatures 0–180ºC and for salinities 0–226 g/kg. Figure 28 depicts this.
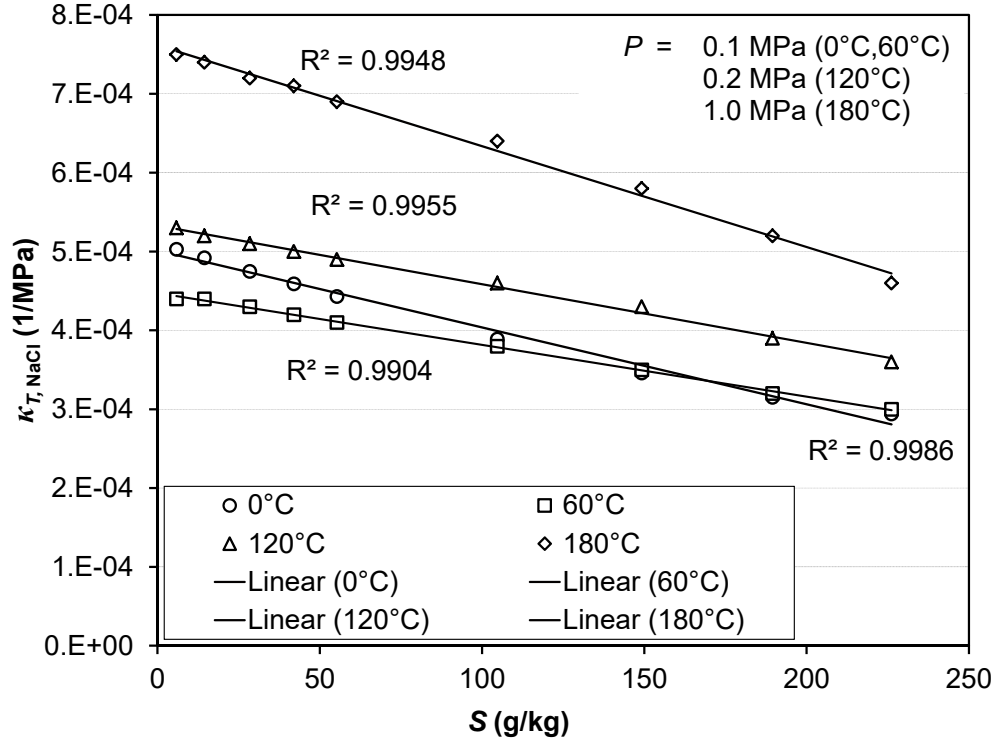
Figure 28. Aqueous sodium chloride isothermal compressibility data of Rogers and Pitzer [45] fit to lines of constant temperature and pressure.

To verify that a linear relationship between isothermal compressibility and salinity, developed solely using data until a salinity of 50 g/kg, can accurately predict compressibility up to high salinities ($50 \leq S \leq 160$ g/kg), the percentage deviation between the data and the relationship was evaluated. Aqueous sodium chloride isothermal compressibility data from Rogers and Pitzer [45] for the range ($0 \leq t \leq 180$ °C; $0 \leq S \leq 55$ g/kg; $0.1 \leq P \leq 20$ MPa) was fit to the following correlation:

$$\kappa_{T,\text{NaCl}} = \kappa_{T,\text{w}} + S \times (b_1 + b_2 t + b_3 t^2 + b_4 P) \tag{54}$$

where, $\kappa_{T,\text{w}}$ was obtained from Eq. (17) and,

$b_1 = -1.0803 \times 10^{-6}, b_2 = 9.8395 \times 10^{-9}, b_3 = -5.5738 \times 10^{-11}, b_4 = 3.5604 \times 10^{-9}$, and the percentage deviation between isothermal compressibility data and the correlation was then evaluated. This is depicted in Fig. 29. The maximum percentage deviations were 1.3 %, 2.5 %, 4.7 % and 15.4 % for salinities less than 56 g/kg, 105 g/kg, 150 g/kg and 226 g/kg respectively. Thus Eq. (54) **Error! Reference source not found.** is accurate to within 5 % until a salinity of 150 g/kg. To further verify that the maximum deviation or maximum error between isothermal compressibility data and that calculated from Eq. **Error! Reference source not found.**(54) scales linearly with salinity, the maximum deviations for the same salinity ranges were calculated. These were found to be 6.4×10^{-6}, 8.7×10^{-6}, 15×10^{-6} and 25×10^{-6} MPa^{-1}; suggesting a strongly linear relationship for the maximum deviation. For seawater, a similar behavior may be expected since the primary constituent of seawater is sodium chloride. Thus, we expect that isothermal compressibility data for seawater until a salinity of 56 g/kg can be used to accurately predict both the compressibility and the maximum error in the prediction up to high salinities ($56 \leq S \leq 160$ g/kg).
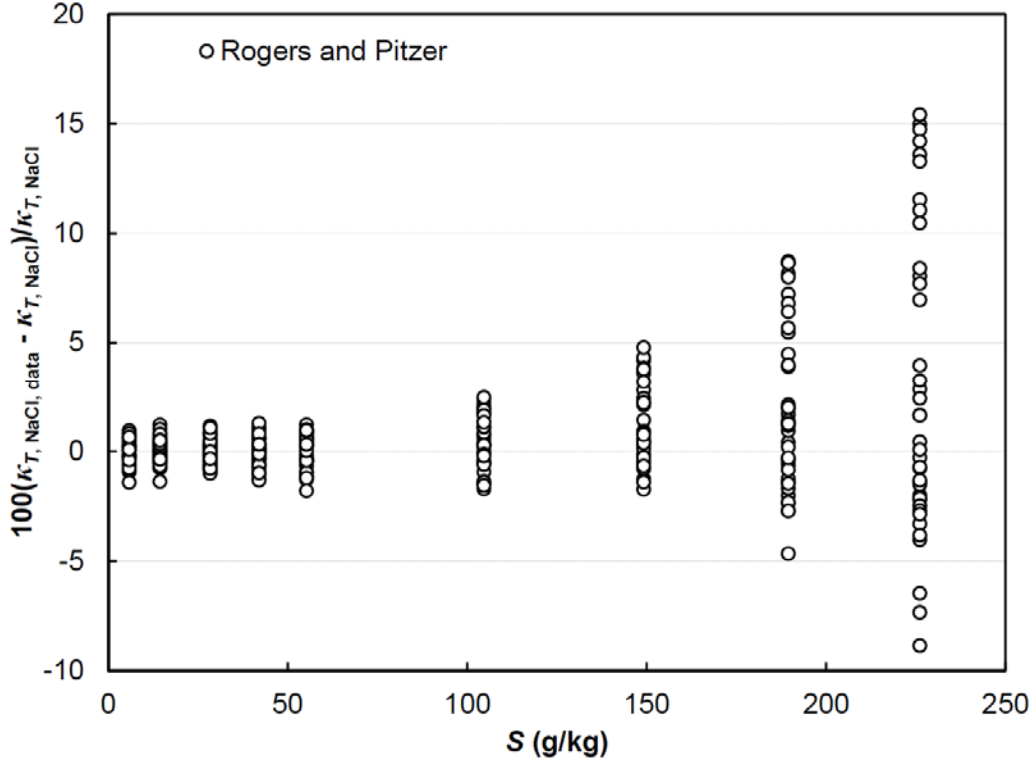
Figure 29. Deviation of isothermal compressibility data of Rogers and Pitzer [45] from Eq. (54)**Error! Reference source not found.**.

A.2 Estimation of uncertainty in isothermal compressibility of seawater at high salinity

To address the second question of maximum uncertainty of Eq. (16) in the region of extrapolation, a simple statistical analysis was performed. Equation (16) can be considered as a family of lines of constant temperature (t_i) and pressure (P_j) with the form:

$$\kappa_{T,\mathrm{sw}}(S,t_i,P_j) = \kappa_{T,\mathrm{w}}(t_i,P_j) + S \times (b_1 + b_2 t_i + b_3 t_i^2 + b_4 P_j) \qquad (55)$$

The actual value for seawater isothermal compressibility can also be considered to have a similar form with intercept $a(t_i,P_j)$ and a slope $b(t_i,P_j)$:

$$\kappa_{T,\text{sw, actual}}(S,t_i,P_j) = a(t_i,P_j) + S \times b(t_i,P_j) \tag{56}$$

Thus, the deviation between data for the isothermal compressibility of seawater and compressibility calculated from Eq. (16) at temperature (t_i) and pressure (P_j) can then be represented as:

$$
\begin{aligned}
\epsilon(\kappa_{T,\text{sw}}(S,t_i,P_j)) &= \kappa_{T,\text{sw, actual}}(S,t_i,P_j) - \kappa_{T,\text{sw}}(S,t_i,P_j) \\
&= a(t_i,P_j) - \kappa_{T,\text{w}}(t_i,P_j) + S \times \left[b(t_i,P_j) - b_1 + b_2 t_i + b_3 t_i^2 + b_4 P_j \right] \\
&= \epsilon_{\text{intercept}}(t_i,P_j) + S \times \epsilon_{\text{slope}}(t_i,P_j)
\end{aligned}
\tag{57}
$$

Analysis of the primary data showed that the error in the slope contributed significantly more than the error in the intercept to the deviation between data and compressibility calculated using Eq. (16). The reason for the slope error being significant is because the pure water part of Eq. (16) was correlated with data accurately to within 0.29 % for temperatures up to 180 °C and pressures up to 12 MPa. Thus, the deviation can be simplified further as:

$$\epsilon(\kappa_{T,\text{sw}}(S,t_i,P_j)) \approx S \times \epsilon_{\text{slope}}(t_i,P_j) \tag{58}$$

The line corresponding to the maximum deviation in slope was found to be at $t_i = 0$ °C and $P_j = 20$ MPa, with the maximum deviation from primary data, $\epsilon_{\text{max,data}}(\kappa_{T,\text{sw}}) = -1.5 \times 10^{-5}$ MPa^{-1} (or -3.47%), at $S = 56$ g/kg. Extending this line to $S = 160$ g/kg gave a conservative estimate of the maximum deviation in the extrapolated region, $\epsilon_{\text{max,extrap.}}(\kappa_{T,\text{sw}}) = 4.4 \times 10^{-5}$ (or 13.36%). This is also shown by the dashed line in Fig. 30. The maximum deviation thus calculated, was taken to be the maximum uncertainty of Eq. (16) in the extrapolated region.

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Figure 30 shows the analysis in a graphical format. Smoothed seawater isothermal compressibility data from Safarov et al. [5,37] is plotted with values from the correlation given in Eq. (16) across salinities 0–160 g/kg at temperatures 0, 60, 120 and 180 °C and at a pressure of 20 MPa. Shown also is the maximum deviation from Eq. (16) in the region of primary data and in the region of extrapolation, as well as a line corresponding to the maximum deviation slope.

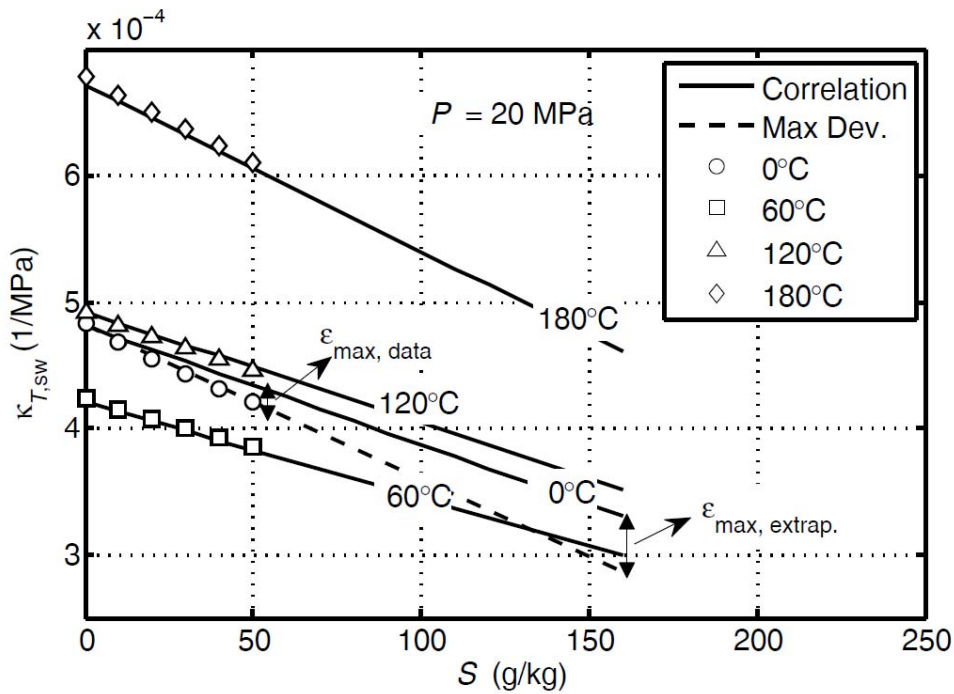Figure 30. Comparison of seawater isothermal compressibility smoothed data points from Safarov et al. [5,37] with values from the correlation given in Eq. (16) across salinities 0–160 g/kg at temperatures 0, 60, 120 and 180 °C and at a pressure of 20 MPa along with a representation of the maximum deviation of the data from Eq. (16) in the

region of primary data and in the region of extrapolation.

Appendix B: Estimation of uncertainty in isobaric expansivity of seawater at high salinity

Experimental data for the isobaric expansivity of seawater was available only until a salinity of 56 g/kg [5]. For salinities greater than 56 g/kg, a method needed to be devised to estimate the uncertainty in the correlation for the isobaric expansivity of seawater, given in Eq. (21). The approach used to estimate the uncertainty in isothermal compressibility of seawater, given in Appendix A, could not be used for isobaric expansivity as expansivity was not found to vary linearly with salinity. This non-linearity was verified by analyzing data on the isobaric expansivity of aqueous sodium chloride reported by Rogers and Pitzer [45] for a wide range of temperature, salinities, and pressures ($0 \leq t \leq 300$ °C; $0 \leq S \leq 226$ g/kg; $0.1 \leq P \leq 100$ MPa) and, by analyzing seawater data reported by Safarov et al. [5]. The only alternative we saw to obtain an upper bound on the uncertainty in this range ($S > 56$ g/kg) was by comparing values obtained from the correlation for isobaric expansivity of seawater developed in this work, given in Eq. (21) to data on aqueous sodium chloride published by Rogers and Pitzer [45]. The comparison was performed for the range $10 \leq t \leq 180$ °C, $0 \leq S \leq 150$ g/kg and $0 \leq P \leq 12$ MPa. The percentage deviations between these are shown in Fig. 31. The MAPD was 18.30 % at $t = 10$ °C, $S = 105$ g/kg and $P = 0.1$ MPa. This was considered to be the maximum uncertainty of Eq. (21) for $S > 56$ g/kg. For engineering applications, the approximation proposed should be acceptable given that sodium chloride is the primary consistent of sea salt and that there is no other better alternative (lack of experimental data and robust thermodynamic models that can extend to high temperature, salinity and pressure).
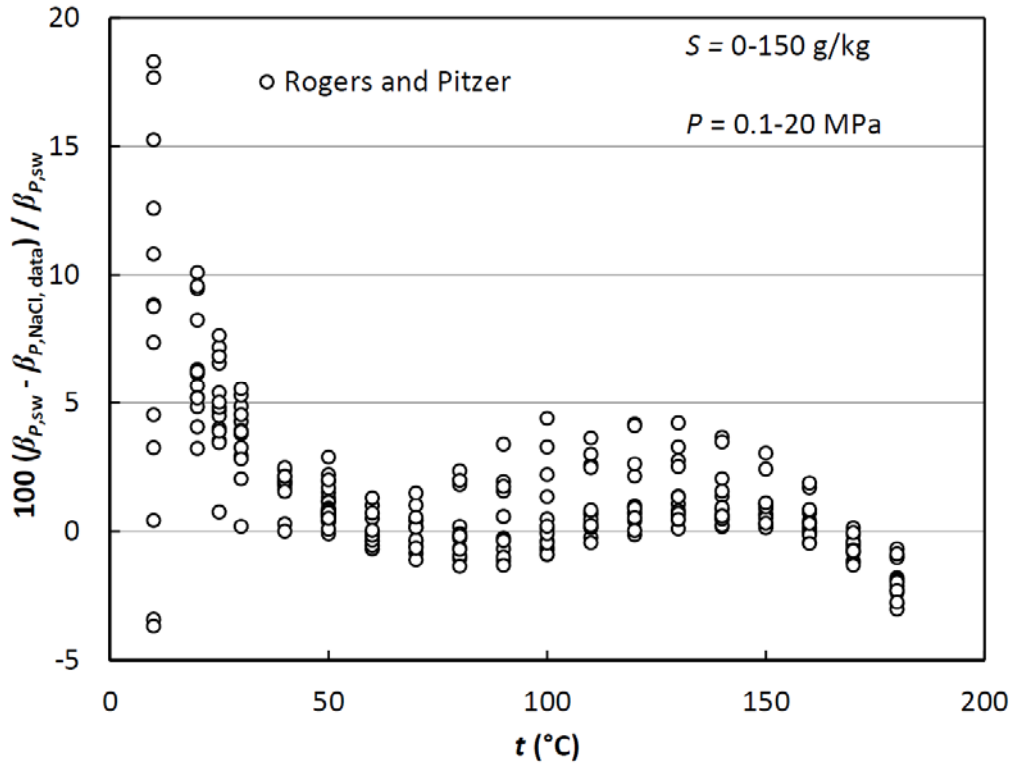
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Figure 31. Percentage deviation of isobaric thermal expansivity data of Rogers and Pitzer [45] from Eq. (21).

Appendix C: Vapor pressure of "Ca-free" artificial seawater

Vapor pressure of seawater is dependent on the composition of seawater. To suppress scale formation, calcium ions are sometimes removed from seawater using chemical treatment. The vapor pressure for "Ca-free" seawater is slightly different from that of natural seawater. Grunberg [31] had published data on the vapor pressure of "Ca-free" artificial seawater. This dataset was selected as "primary data" for developing a correlation for the vapor pressure of "Ca-free" artificial seawater. The data on the vapor pressure of natural seawater by Grunberg [31] and other datasets by Robinson [29], Emerson and Jamieson [30] and Sharqawy et al. [2] were considered as "secondary" for comparison purposes. The datasets are summarized in Table 15.

Table 15. Data for "Ca-free" artificial seawater vapor pressure.

Ref.	Year	Seawater type	t (°C)	S (g/kg)	$u_c(p_v)/p_v$ (%)
Primary					
Grunberg [31]	1970	Ca-free artificial	20–180	0–160	0.07
Secondary					
Grunberg [31]	1970	Natural	20–180	0–160	0.07
Robinson [29]	1954		25	18–40	0.02
Emerson [30]	1967	Synthetic	100–180	32–145	0.07
Sharqawy[2]	2010	Raoult's Law			

Primary data was used to obtain the best-fit correlation for the vapor pressure of "Ca-free" natural seawater:

$$\ln\left(p_{v,sw} / p_{v,w}\right) = -4.2182 \times 10^{-4} S - 1.7817 \times 10^{-6} S^2 \tag{59}$$

where, $p_{v,w}$ is the vapor pressure of pure water in Pa obtained from Sharqawy et al. [2] and S is salinity in g/kg. The correlation is valid across a temperature range of $t = (20 - 180)$ °C and a salinity range of $S = (0 - 160)$ g/kg. The MAD from primary data was 0.29 % while the average absolute percentage deviation was 0.06 %. The maximum uncertainty of Eq. (59) was thus 0.29 %. The deviations from Grunberg's data as well as other datasets are depicted in Fig. 32. It can be seen that, for the same salinities, the vapor pressure of natural seawater deviates from that of "Ca-free" seawater by up to 1.5 %.
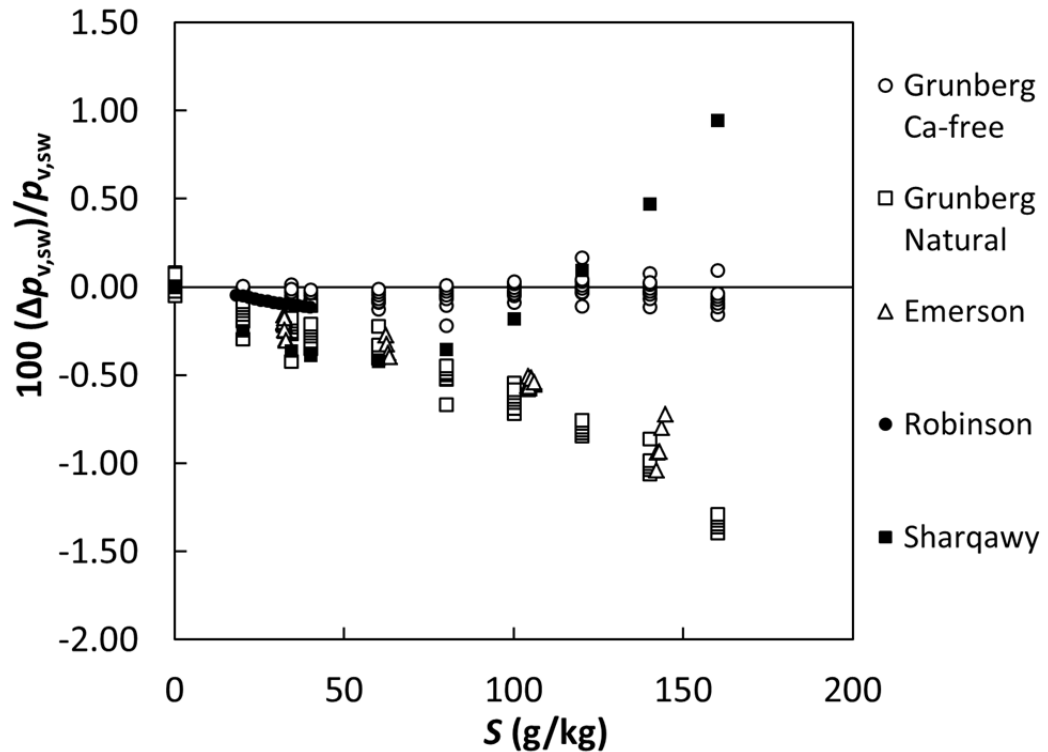

Figure 32. Deviation of literature data on vapor pressure of seawater from values for the vapor pressure of "Ca-free" artificial seawater given in Eq. (59).

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Appendix D Activity of water in seawater

The activity of water in seawater is a property which is used widely in marine chemistry applications. This property is typically derived from a thermodynamic model such as Pitzer's [65], with the model itself fit to vapor pressure data or boiling point elevation data. In the literature, the activity of water in seawater was reported previously by Bromley et al. [33] and by Lund et al. [66]. Bromley et al., calculated activity using a model fit to boiling point elevation data and reported data for $0 \leq t \leq 200$ °C and $10 \leq S \leq 120$ g/kg while Lund used statistical mechanics to calculate activity for $t = 25$ °C and $5 \leq S \leq 35$ g/kg.

For sufficiently low pressures, the activity of water in seawater can be approximated by the vapor mole fraction:

$$a_{w,sw} = p_{v,sw} / p_{v,w} \tag{60}$$

where $p_{v,\,sw}$ was calculated using Eq.(5) and $p_{v,\,w}$ using Eq.(6). To verify the accuracy of the approximation, data on the activity of water in seawater from Bromley et al. was compared with activity obtained using Eq. (60) for $0 \leq t \leq 180$ °C and $10 \leq S \leq 120$ g/kg. The percentage deviations between these are shown in Fig. 33. The MAD was 1.56 %; this was considered to be the maximum uncertainty of the expression for the activity of water in seawater. The results of the analysis are also summarized in Table 16.
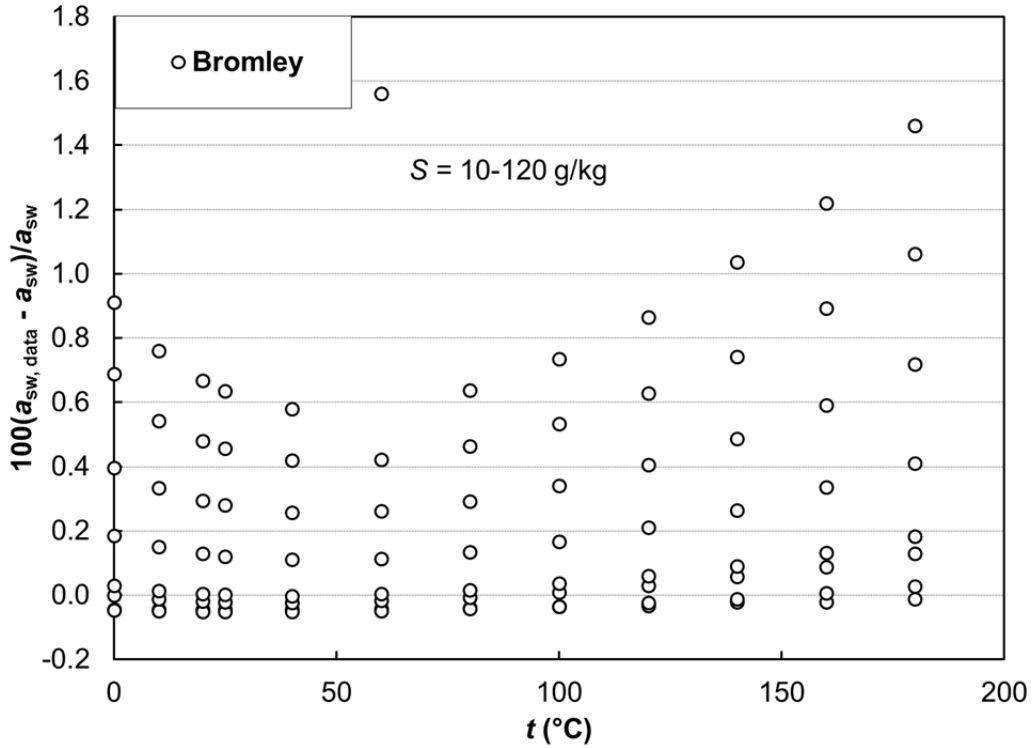
Figure 33. Percentage deviation of activity of water in seawater calculated using the relationship, given by Eq. (60), from Bromley et al.'s reported data for [33] $0 \leq t \leq 180$ °C and $10 \leq S \leq 120$ g/kg.

Table 16. Activity of water in seawater.

Equations
$a_{w,sw} = p_{v,sw} / p_{v,w}$
where, $p_{v,\,sw}$ and $p_{v,\,w}$ are from Eqs. (5) and (6)

Range of validity and maximum uncertainty: $a_{w,sw}$ in (-);

Range	U_{max}

Literature	$0 \leq t \leq 180\ °C;\ 0 \leq S \leq 120$ g/kg; $P = p_{v,\ sw}$	1.56 %
data	Ref: [33]	

Appendix E: Internal consistency and colligative properties

When thermophysical properties are individually correlated against raw data, perfect internal consistency between each property is not typically possible. Perfect internal consistency requires all properties to be derived from a single function. However, as long as correlations are accurate and internally consistent to within reasonable bounds, they may be used without any problems in engineering applications. In this section, the internal consistency between properties, the recommended expressions for property calculation and the inaccuracies arising from select expressions are discussed. The "recommended use" and "not recommended use" for select expressions are summarized in Table 17 along with the accuracies of the expression in both regions where literature data is available as well as where an extrapolation was used.

E.1 $c_{P,\mathrm{sw}}, h_{\mathrm{sw}}, s_{\mathrm{sw}}$ and g_{sw}

For specific: heat capacity, enthalpy, entropy and Gibbs energy of seawater, the expressions for recommended use are Eqs. (22), (25), (29) and (36), developed in this paper. Values of enthalpy, entropy and Gibbs energy are consistent with specific heat capacity to within the maximum uncertainty bounds mentioned in this paper. Directly differentiating correlations for enthalpy, entropy and Gibbs energy to calculate specific heat capacity, density and isobaric expansivity is generally not recommended, as the correlations are simple polynomials fit to data. In case they are differentiated, it is recommended that values obtained by differentiation be compared with direct correlations developed in this paper before use, to ascertain the inaccuracy arising from differentiation.

Gibbs energy, enthalpy and entropy can also be expressed as thermodynamic functions of each other, such that any two properties can be used to calculate the third:

$$g_{sw,h,s} = h_{sw} - Ts_{sw} \tag{61}$$

$$h_{sw,g,s} = g_{sw} + Ts_{sw} \tag{62}$$

$$s_{sw,g,h} = (h_{sw} - g_{sw})/T \tag{63}$$

Maximum uncertainty bounds for these expressions were obtained by comparing with raw data from IAPWS-08 equation of state for seawater and with thermodynamic formulations expressing these properties as a function of specific heat capacity of seawater—the same approach used while developing the direct correlations. The exact values are listed in Table 17. The analysis showed that direct polynomial correlations for each of the three properties gave values that were more accurate than if a third property was calculated from the other two. Expressing Gibbs energy in the form given by Eq. (61) as $g_{sw,h,s}$ is strongly not recommended due to magnification of errors as g approaches zero near $t = 40\ °C$. This was discussed in detail in Section 10. Enthalpy and entropy may be expressed respectively as $h_{sw,g,s}$ and $s_{sw,g,h}$ but these are less accurate than the direct correlations by approximately 1 % at elevated pressures.

E.2 ϕ_{sw} and a_{sw}

The expressions for recommended use for osmotic coefficient, activity of water in seawater and vapor pressure of seawater, are Eqs. (40), (60) and (5). They are however interrelated and can be expressed as functions of each other. Of these three properties, osmotic coefficient is the most widely used in desalination applications. Hence, the analysis reported here looks at how osmotic

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coefficient could be expressed as a function of activity of water in seawater and the maximum uncertainty of these expressions.

The osmotic coefficient as a function of activity of water in seawater is given by:

$$\phi_{sw,a} = \frac{-\ln(a_{w,sw}) \times 1000 \times m_s}{MW_w} = \frac{-\ln(a_{w,sw}) \times (1000 - S) \times MW_s}{MW_w \times S} \tag{64}$$

where, $a_{w,sw}$ is given in Eq. (60), m_s is the concentration of sea salt expressed in units of molality (mol/kg) and MW_w is the molecular weight of pure solvent. Expressing the concentration in units of salinity we get:

$$\phi_{sw,a} = \frac{-\ln(a_{w,sw}) \times (1000 - S) \times MW_s}{S \times MW_w} \tag{65}$$

where MW_s is 31.4038 g/mol, the effective molar mass of sea salt [14].

Maximum uncertainty bounds for both expressions of osmotic coefficient were obtained by comparing with raw data from IAPWS-08 equation of state for seawater with the results listed in Table 17. Osmotic coefficient obtained from the activity of seawater with a MAPD of 25.14 % for $0 \leq S \leq 10$ g/kg and a MAPD of 9.86 % for $10 < S \leq 120$ g/kg, was less accurate than that from Eq. (40) especially at low salinities.

Table 17. Summary of accuracies for select seawater properties according to how they are expressed, with "recommended" and "not recommended" forms distinguished

Variable	Recommended form	Not recommended form
Example:	Eq. A	Eq. B
x_{sw}	Maximum uncertainty in region of	Maximum uncertainty in region of literature

	literature data (Maximum uncertainty in extrapolated region)	data (Maximum uncertainty in extrapolated region)
h_{sw}	Eq. (25) 1.36 % (1.47 %)	$h_{sw,g,s} = g_{sw} + Ts_{sw}$ 1.42 % (3.17 %)
s_{sw}	Eq. (29) 0.50 % (1.47 %)	$s_{sw,g,h} = (h_{sw} - g_{sw})/T$ 1.27 % (2.62 %)
g_{sw}	Eq.(36) 0.07 kJ/kg (0.11 kJ/kg)	$g_{sw,h,s} = h_{sw} - Ts_{sw}$ 0.36 kJ/kg (> 0.36 kJ/kg)
ϕ_{sw}	Eq. (40) and (41) 2.57 % (0.89 %)	$\phi_{sw,a} = \dfrac{-\ln(a_{w,sw}) \times (1000 - S) \times MW_s}{S \times MW_w}$ 9.86 % (25.14 %)

Appendix F: Pure water properties

Correlations presented in this paper for the thermophysical properties of seawater can be used to calculate the thermophysical properties of pure water by setting the salinity *S* to 0 g/kg. The correlations are in general more accurate for calculating pure water properties than when used to calculate seawater properties. For the benefit of the readers, the maximum uncertainty and validity range when the seawater correlations in this paper are used to calculate pure water properties is summarized in Table 18. The maximum uncertainty was calculated by comparing the values from the correlations with reference pure water datasets. The datasets used for each correlation is also reported in Table 18. To the best of the knowledge of the authors, simple polynomial based pressure dependent correlations for individual pure water properties have not been comprehensively listed together elsewhere in the literature. We expect Table 18 and the associated correlations to be useful to the wider engineering community for calculating pure water properties easily.

The pure water properties summarized are for isothermal compressibility (Eq.(17)), density (Eq. (18)), isobaric thermal expansivity (Eq.(21)), isobaric specific heat capacity (Eq. (22)), enthalpy (Eq. (25)), entropy (Eq. (29)), Gibbs energy (Eq. (36)), thermal conductivity (Eq. (51)) and surface tension (Eq.(52)). With the exception of surface tension, all other correlations include the effect of pressure.

Table 18. Maximum uncertainty and validity range when seawater property correlations presented in this paper are used to calculate properties of pure water with the references used for

obtaining uncertainty cited.

Property	Units	Validity range	U_{max}	Ref.
$\kappa_{T,\text{sw}}(t, 0\text{ g/kg}, P)$	MPa^{-1}	$0 \le t \le 180\ °\text{C}$; $0 \le P \le 12$ MPa;	± 0.29 %	[46]
$\rho_{\text{sw}}(t, 0\text{ g/kg}, P)$	kg/m^3	$0 \le t \le 180\ °\text{C}$; $0 \le P \le 12$ MPa;	± 0.02 %	[46]
$\beta_{P,\text{sw}}(t, 0\text{ g/kg}, P)$	K^{-1}	$10 \le t \le 180\ °\text{C}$; $0 \le P \le 12$ MPa;	± 8.76 %	[46]
$c_{P,\text{sw}}(t, 0\text{ g/kg}, P)$	J/kg-K	$0 \le t \le 180\ °\text{C}$; $0 \le P \le 12$ MPa;	± 0.23 %	[46]
$h_{\text{sw}}(t, 0\text{ g/kg}, P)$	J/kg	$10 \le t \le 150\ °\text{C}$; $0 \le P \le 12$ MPa;	± 0.11 %	[46]
$s_{\text{sw}}(t, 0\text{ g/kg}, P)$	J/kg-K	$10 \le t \le 150\ °\text{C}$; $0 \le P \le 12$ MPa;	± 0.11 %	[46]
$g_{\text{sw}}(t, 0\text{ g/kg}, P)$	J/kg	$10 \le t \le 150\ °\text{C}$; $0 \le P \le 12$ MPa;	± 0.03 kJ/kg	[46]
$k_{\text{sw}}(t, 0\text{ g/kg}, P)$	W/m-K	$0 \le t \le 99\ °\text{C}$; $P = P_0$	± 0.06 %	[34,55]:
	W/m-K	$0 \le t \le 99\ °\text{C}$; $0.1 \le P \le 140$ MPa	± 1.1 %	[55]
$\gamma_{\text{sw}}(t, 0\text{ g/kg}, P)$	mN/m	$1 \le t \le 370\ °\text{C}$; $P = P_0$	± 0.5 %	[62]: