



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



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## HIGHLIGHTS

- New pressure-dependent correlations for seawater properties:  $\kappa$ ,  $\beta$ ,  $\rho$ ,  $c_p$ ,  $h$ ,  $s$  and  $g$
- Correlations are valid for:  $t = 10\text{--}120\text{ }^\circ\text{C}$ ,  $S = 0\text{--}120\text{ g/kg}$  and  $P = 0\text{--}12\text{ MPa}$ .
- New correlations for seawater properties:  $p_v$ ,  $k$ , and  $a_w$
- Review of recent work on seawater properties:  $\gamma$ ,  $\varphi$ , and  $\pi$
- Uncertainty bounds predicted using thermodynamics and statistical methods

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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 ( $P = 0.1\text{--}12\text{ MPa}$ ) 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:  $t = 0\text{--}120\text{ }^\circ\text{C}$ ,  $S = 0\text{--}120\text{ g/kg}$ , and  $P = 0\text{--}12\text{ MPa}$ . 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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## 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 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

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## Nomenclature

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

### Greek symbols

$\beta_p$	isobaric thermal expansivity $\text{K}^{-1}$
$\gamma$	surface tension $\text{mN m}^{-1}$
$\kappa_T$	isothermal compressibility $\text{MPa}^{-1}$
$\pi$	osmotic pressure MPa
$\rho$	density $\text{kg m}^{-3}$
$\varphi$	osmotic coefficient

### Subscripts

s	sea salt
sw	seawater
w	pure water

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 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 a 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:  $4 \leq t \leq 40 \text{ }^{\circ}\text{C}$ ,  $0 \leq S \leq 42 \text{ g/kg}$  and  $0 \leq P \leq 100 \text{ MPa}$ . 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.

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:  $-10 \leq t \leq 80 \text{ }^{\circ}\text{C}$ ,  $0 \leq S \leq 120 \text{ g/kg}$  and  $0 \leq P \leq 100 \text{ MPa}$ . For near atmospheric pressures, IAPWS-08 was valid for:  $-2 \leq t \leq 80 \text{ }^{\circ}\text{C}$  and  $0 \leq S \leq 120 \text{ g/kg}$ . Here, near atmospheric pressures refers to atmospheric pressure for temperatures less than the boiling point of seawater ( $t < 100 \text{ }^{\circ}\text{C}$ ), 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:  $-2 \leq t \leq 40 \text{ }^{\circ}\text{C}$ ,  $0 \leq S \leq 42 \text{ g/kg}$  and  $0 \leq P \leq 100 \text{ MPa}$ . 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  $80 \text{ }^{\circ}\text{C}$  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

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