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Physicochemical, transport and thermodynamic properties of saline solutions for process design using Padé approximants

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ABSTRACT

Padé approximants are used to model physicochemical, transport, and thermodynamic properties of seawater for industrial applications. Sophisticated mathematical models to calculate saline solution properties are presented in the literature for applications in which very high accuracy is needed, such as oceanographic studies. Such accuracy is not necessary in the design and optimization of processes in which seawater is used, mainly in the mining industry (mineral concentration, hydrometallurgy, and refining processes). The properties studied are density, specific heat, osmotic coefficient, viscosity, thermal conductivity, surface tension, enthalpy, entropy, vapor pressure, latent heat of vaporization, and boiling temperature elevation. Padé approximants represent a useful tool in applied mathematics and have not been used to model saline solutions properties in the way presented here. Padé results are compared with Taylor series and simple polynomial expansions. The general models obtained are of rational type and give deviations similar to those provided by more sophisticated models presented in the literature.

Keywords: Seawater properties; Padé approximants; Taylor series; Density; Transport properties; Thermodynamic properties

1. Introduction

Water is the most universal good in our daily life and in the industry, and in both areas the demand for this resource increases day by day due to the increase in population and due to the rapid industrial development in many countries [1]. Water scarcity is one of the main challenging problems in industry, but it is of special relevance in mineral processes in which water consumption is huge and also because mining operations are usually located where there is no water or water is extremely scarce. Although the amount of water used per kilogram of mineral produced varies from mine to mine and also through the years, an average estimate can be done. One report on water consumption in copper production indicates that between 200 and 500 L of water are used to produce one kilogram of mineral [2]. Part of the water used in a process is treated and recirculated, but still the amount of fresh water needed is not easily available in nature. Under this scenario, most of the new mining projects consider the use of seawater or

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desalinated water to partially supply their needs, and at present, most mining countries make use of seawater in their mining operations.

The main problem in using seawater in industry is the salt content that may affect some processes. The global concentration of salts in seawater varies between narrow ranges (34–37 g of salts per kilogram of solution) but important local variations (where seawater is collected for a given process) may occur and salinity and temperature of seawater could also vary in a significant way, affecting the value of its thermophysical properties [3]. Perhaps more important is that during industrial processes in which seawater is used, temperature and salinity may change and, therefore, properties of the solution will also change. Therefore, accurate data for seawater properties are needed as function of temperature and salinity. Experimental data of seawater properties are available, but the data are dispersed in the literature, are incomplete or are available for ranges of temperature and salinity outside the ranges of interest in industrial processes. Also, obtaining experimental data for all situations required in industrial processes is very expensive. For process equipment design, for material and energy balances and for simulation processes it is convenient to express the variation of seawater properties with temperature and salinity using accurate mathematical models. Good-accurate models are obtained using good-accurate data [4].

The availability of good-accurate data will clearly have economic benefits since good data would allow: (1) improving process conditions; (2) developing new processes; (3) reducing oversizing in the design of new equipment; and (4) reducing energy requirements [4]. In other situations, aspects related to safety or to environmental issues must be taken into consideration. From an academic point of view, having good accurate data allows corroborating theories and correlations, and completing data bases for multiple purposes.

In oceanographic studies, differences in salinity of 10^{-5} to 10^{-6} g of salt per kilogram of solution have usually very small influence in the calculation of some properties of seawater. However, such small differences may cause erroneous results and erroneous conclusions about certain phenomena occurring in the sea. For instance, in the determination of density field, density values are of crucial importance, since density plays an important role in determining where the water will flow. For industrial applications on the surface of the Earth, such very accurate measurements and estimates are not necessary. Therefore, the interest in this work is on the proposal of simple models for estimating seawater properties within accuracies of common instruments and within errors of experimental data in industrial processes; in a rough general way, absolute deviations of the order of 0.1–1%.

The estimation of physical, chemical, and thermodynamic properties of seawater is not an easy problem to solve, considering that seawater from different places have different temperature and salt content and even may have different type of salts. However, there are some concepts and assumptions that have been developed to simplify engineering calculations. The definition of the reference salinity concept, for instance, is one of the major contributions and can be used in process design and process simulation. In a simple way, salinity is a measure of the dissolved solids in seawater, usually expressed in grams of salt per kilogram of solution.

Seawater properties such as density, specific heat, osmotic coefficient, viscosity, thermal conductivity, surface tension, enthalpy, entropy, vapor pressure, latent heat of vaporization, and boiling temperature elevation are widely required in several calculations, such as pumping, fluid flow, evaporation, flotation, leaching, reverse osmosis, solvent extraction, and crystallization, among others. Several models for these seawater properties have been proposed through the years. A good recent compilation of selected models has been presented by Sharqawy et al. [5]. These authors recommend using the models that gives the lowest average deviation between calculated and experimental data, independent of the complexity of the model. For those recommended models, deviations are very low, so values calculated by these models can be considered as pseudo experimental data and are used in this work.

In all regression analysis, the optimum values of the model parameters are those that optimize a chosen objective function. Such an objective function must include the experimental data and the model estimates, being the most common expressions for such objective functions the difference between the values calculated with the model and the experimental data, in absolute values, squared differences, root square of differences, and other more involved definitions. From the practical point of view, however, there are three statistical parameters that according to literature, studies are the most appropriate ones for deciding about the goodness and accuracy of a mathematical model: the mean average deviation, the mean average absolute deviation, and the maximum absolute deviation, as detailed later in this paper [6].

Padé approximants are useful tools in applied mathematics and have been frequently used in statistical mechanics, thermodynamics, and estimation of physical properties [7–10] but has not been applied to correlate and estimate properties of seawater as proposed here. In this work, application of Padé approximants is done to correlate the following properties of seawater: density, specific heat, osmotic coefficient, viscosity, thermal conductivity, surface tension, enthalpy, entropy, vapor pressure, latent heat of vaporization, and boiling temperature elevation.

2. Formulation

2.1. Models for seawater properties

As described above, there are several models proposed in the literature for different properties at different ranges of temperature (T) and salinity (S). Although properties vary in a regular, smooth form with these variables, the combined effect (of T and S) is different for different properties. This has given origin to the proposal of sophisticated algebraic expression with high number of adjustable parameters, including high degree polynomials, potential functions, and logarithmic functions, among others. For example a third degree polynomial in T and a second degree polynomial in S with a total of 12 adjustable parameters for the specific heat of seawater at a temperature T and total salinity S has been proposed [5]:

$$C = [a_0 + a_1 S + a_2 S^2] + [b_0 + b_1 S + b_2 S^2] \cdot T + [c_0 + c_1 S + c_2 S^2] \cdot T^2 + [d_0 + d_1 S + d_2 S^2] \cdot T^3 \tag{1}$$

For the viscosity a logarithmic-type model containing 14 parameters, is recommended [5]:

$$\begin{aligned}\log(\mu) = {} & \log\left[a_1 + \left\{(a_2(\mathrm{t} + a_3)^2 + a_4\right\}^{-1}\right] + b_1\left[\frac{c_1 S}{1 + c_2 S}\right] \\ & + b_2\left[\frac{c_1 S}{1 + c_2 S}\right]^2 + b_3\left[\frac{c_1 S}{1 + c_2 S}\right]^3 \\ & + \log\left[a_1 + \left\{(a_2(\mathrm{t} + a_3)^2 + a_4\right\}^{-1}\right] \\ & \times \left\{b_4\left[\frac{c_1 S}{1 + c_2 S}\right] + b_5\left[\frac{c_1 S}{1 + c_2 S}\right]^2 + b_6\left[\frac{c_1 S}{1 + c_2 S}\right]^3\right\}\end{aligned} \tag{2}$$

For the thermal conductivity, an expression containing logarithmic terms, potential terms, and rational expressions, with a total of nine parameters, has been proposed [5]:

$$\log(k) = \log(a_1 + a_2 \cdot S) + a_3\left[a_4 - \frac{a_5 + a_6 \cdot S}{T}\right]\left[1 - \frac{T}{a_7 + a_8 \cdot S}\right]^{a_9} \tag{3}$$

As observed, these expressions (1–3) seem to be somewhat complex for properties that have smooth behavior with the independent variables T and S, as shown in Fig. 1. As shown in the figure, in the range of temperature and salinity considered in this study, the effect of temperature is more important for viscosity than for the other properties (specific heat and thermal conductivity). The values for the viscosity

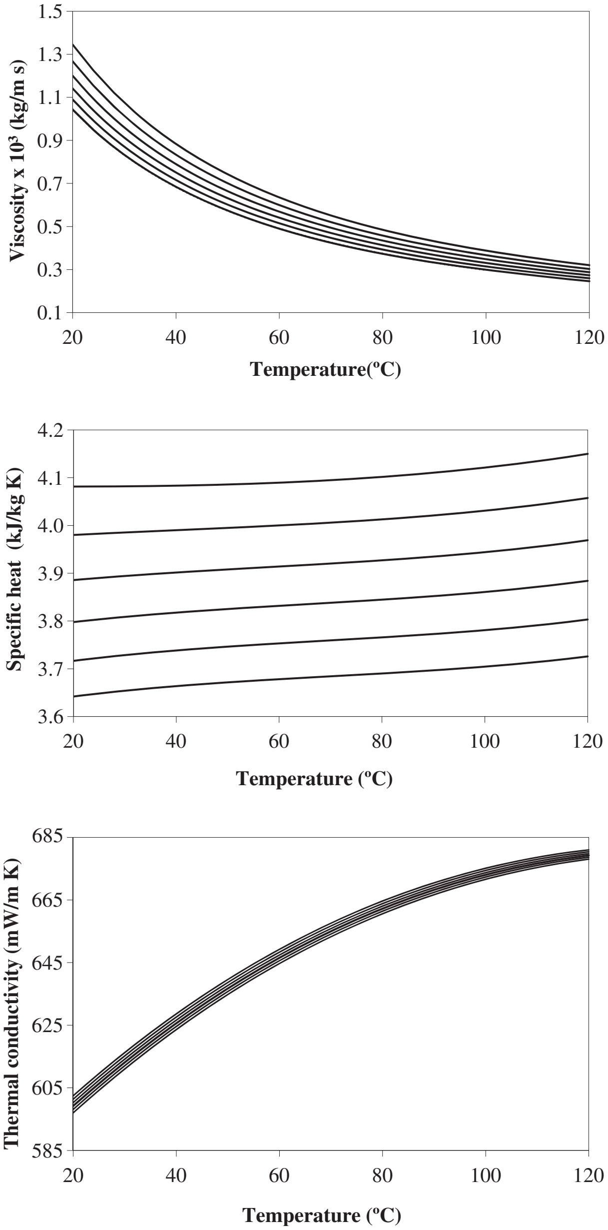

Fig. 1. Viscosity, specific heat, and thermal conductivity of seawater as a function of temperature and salinity. Salinity is 20, 40, 60, 80, 100, and 120 g/kg, from bottom to top in viscosity and from top to bottom for specific heat and thermal conductivity.

vary up to four times (from about 0.3–1.3 kg/m s), while for specific heat and thermal conductivity values change by about 10–15% in the same range of temperature and salinity. The effect of salinity is low in all cases being also higher for the viscosity (50% variation at lower temperatures).

Table 1 presents selected models for several properties of seawater as recommended by Sharqawy et al. [5]. In the table, models are classified in an arbitrary but convenient way as: Lin = linear, Pol = polynomial, Log = logarithmic, Rat = rational, and Pot = potential. The symbol * indicates that the model includes the pressure as an independent variable. As seen in the table, not only equations are complex for the specific heat, the viscosity, and the thermal conductivity as shown above, but also for density (polynomial-type with 24 parameters) and surface tension (potential-type with seven parameters). In this context, it seem interesting to take advantage of some of the attractive properties of Padé approximants to propose models that without losing accuracy contain few parameters. It seems that there is no reason that justify having 10 or more parameters for modeling the specific heat, the viscosity, or the thermal conductivity of seawater to obtain the necessary accuracy. Very high accuracy may be required in oceanographic studies but certainly this is not needed for process engineering applications such as those mentioned above in which

Table 1
Summary of correlations proposed in the literature for seawater properties (Pol = Polynomial; Pot = Potential; Rat = Rational; Lin = Linear; and Log = Logarithmic)

Property	Nº par	Math type	Range T	Range S	$\%\Delta y$
Density (ρ)	12	Pol	20–180 (t_{68})	10–160 (S_p)	0.1
	15	Pol + Pot	2–40 (t_{68})	0–42 (S_p)	0.01
	24*	Pol	0–180 (t)	0–180 (S)	2.5
	10	Pol	0–180 (t)	0–160 (S)	0.1
Vapor pressure (p^{vap})	8	Log	100–180 (t_{48})	35–170 (S_p)	0.07
	8	Pol	25 (t_{48})	10–22 (Cl) $^{0}/_{00}$	0.2
	4	Log	273–313 (T_{48})	0–40 (S_p)	0.015
	14	Pol + Pot	0–40 (t_{68})	0–40 (S_p)	0.02
Boiling temperature elevation (BTE)	8	Rac + Pot	273–473 (T_{68})	0–0.12 kg/kg (S_p)	0.1
	6	Pol	20–180 (t_{48})	35–100 (S_p)	0.7
	6	Pol	0–200 (t)	0–120 (S)	1.7
Osmotic coefficient (Ω)	7	Pol	25 (t_{68})	0.016–0.04 kg/kg (S_p)	0.1
	18	Rac + Pot + Log	0–40 (t_{68})	0–0.04 kg/kg (S_p)	0.3
	10	Pol	0–200 (t)	10–120	1.4
Viscosity (μ)	12	Rac + Pot + Log	20–150 (t)	15–130 (S_p)	0.4
	10	Pol	10–180 (t_{68})	0–150 (S_p)	1
	10	Pol	0–180 (t)	0–15 (S)	1.5
Thermal Conductivity (k)	9	Rac + Pot + Log	0–180 (t_{68})	0–160 (S_p)	3
	5*	Log	0–60 (t_{68})	0–60 (S_p)	0.5
	4*	Log	0–30 (t_{68})	35 g/kg (S_p)	0.4
Surface tension (τ)	3	Lin	0–40 (t_{27})	10–35 (S_k)	na
	3	Lin	0–40 (t_{27})	10–35 (S_k)	na
	4	Lin	15–35 (t)	5–35 (S_p)	0.1
	7	Pot + Log	0–40 (t)	0–40 (S)	0.18
Specific heat (C)	12	Pol	273–453 (T_{48})	0–180 (S_p)	0.28
	9	Pol	0–180 (t_{48})	0–12% (S_k)	0.001
	11	Pol	5–35 (t_{68})	0–22 (Cl)	0.01
	20*	Pol	0–374 (t)	0–40 (S)	4.62
Entropy (Ψ)	34*	Pol	0–375 (t)	0–120 (S)	35
	14	Pol + Pot	0–40 (t_{68})	0–40 (S_p)	8
	15	Pol	10–120 (t)	0–0.12 (S)	0.5
Enthalpy (h)	16	Pol + Pot	0–40 (t_{68})	0–40 (S_p)	12
	14	Pol	0–120(t)	0–120(S)	0.5
	7	Pol	0–30 (t_{68})	10–40(S_p)	0.6
Heat of vaporization (Δh^{vap})	5	Pol	0–200 (t)	0–120 (S)	0.01

Source: Data are from Sharkawy et al. [5].

seawater can, partially, or totally, replace potable or natural water (mineral concentration, hydrometallurgy, or refining processes).

2.2. Padé approximants

In 1892, the French mathematician Henri Eugène Padé presented a systematic study on the approximate representation of a function by rational fractions in the Scientific Transactions of the École Normale Supérieure in Paris, representation known nowadays as Padé approximants. These approximants have been used in fluid dynamics [11], in optics [12], in statistical thermodynamics [7,13], in linear circuit analysis [14], in quantum field theory [15], in material behavior [16], and in finance calculations [17] among other applications. Padé approximants have also shown to be a useful tool for correlating properties of substances in particular physical, physicochemical, and transport properties of foods [10]. To the best of the author's knowledge, Padé approximants have not been used to model properties of seawater as function of temperature and salinity.

Padé approximants are rational functions in which the numerator is a polynomial $Q_m(x)$ and the denominator is another polynomial $R_n(x)$. If a set of data is fitted using this rational expression $Q_m(x)/R_n(x)$, known as Padé approximant, the accuracy of the fitted equation would be, in general, much better that a polynomial or an expansion in series such as Taylor or Maclaurin series [18,19]. In other words, one would require many terms in the series to represent the function that a Padé approximant can represent with only few parameters.

Padé approximants are designated with the symbol $P_{m,n}(x)$, as follows:

$$f(x) = P_{m,n}(x) = \frac{Q_m(x)}{R_n(x)} \tag{4}$$

In Eq. (4) $Q_m(x)$ and $R_n(x)$ are polynomials of degree m and n, respectively.

$$\begin{aligned} Q_m(x) &= q_o + q_1 \cdot x + q_2 \cdot x^2 + q_3 \cdot x^3 + \ldots + q_m \cdot x^m \\ R_n(x) &= r_o + r_1 \cdot x + r_2 \cdot x^2 + r_3 \cdot x^3 + \ldots + r_n \cdot x^n \end{aligned} \tag{5}$$

The simplest Padé of a function of a single variable, $f(x)$, is that in which the polynomials Q and R are of first order, as follows:

$$f(x) = \frac{\alpha + \beta \cdot x}{1 + \gamma \cdot x} \tag{6}$$

Press et al. [20] presented an interesting case of a function that clearly shows the advantages of Padé over analytical series expansions or simple fitted polynomials. The function considered was $f(x) = [7 + (a + x)^{4/3}]^{1/3}$. This case is discussed and extended here to clarify the advantages of Padé approximants. Fig. 2 shows the results for this function and three models: polynomial of order four, Taylor series of order four, and a simple $P_{2,1}$.

As observed in Fig. 2, Padé representation is simply remarkable, up to high values of x, much higher than the maximum of the range in which the equations were fitted ($x = 2$). Why Padé behaves this way but sometimes it does not, is until today a mystery for the mathematicians. However, it is generally accepted that it is difficult to know in advance how Padé is going to work and the accuracy will depend on each particular application. Press et al. [20] presented a nice analysis of Padé approximants and wrote:

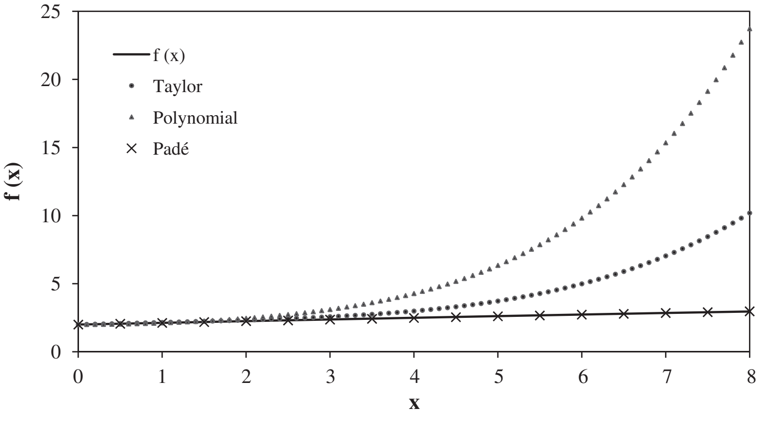

Fig. 2. The function $f(x) = [7 + (a + x)^{4/3}]^{1/3}$ fitted with a polynomial, with a Taylor series and with a Padé expression.

> That is the downside of Padé approximation: it is uncontrolled. There is, in general, no way to tell how accurate it is, or how far out in x it can usefully be extended. It is a powerful, but in the end still mysterious, technique.

There are, of course, several mathematical conditions of the function $f(x)$ to be well represented by a Padé approximant. The most important is that $f(x)$ should be continuous in the range of x for which Padé is going to be applied. Also, Padé approximants are affected by some "anomalies" being one of the most commented in the literature so called "poles" that occurs when the denominator becomes zero [21].

The most common and accurate approximants are those in which the polynomial $Q_m(x)$ has the same degree or one more degree than polynomial $R_n(x)$ [22]. If the ratio $Q_m(x)/R_n(x)$ is expanded in a Taylor or Maclaurin series, one would need in many cases much more terms than $(n + m)$ in the series to give values similar to those of the function being studied. For example, Valderrama and Sandler [7] calculated second virial coefficients using perturbation theory, which is in fact an expansion in series. The authors demonstrated that a simple $P_{2,1}$ model (with three parameters) gives more accurate results than a six degree polynomial.

From a practical point of view, Padé approximants represent a simple form for modeling properties that can be represented by series. This is the case of most of the properties of substances in which these vary in a continuous and monotonous way with certain defined variables. In the applications of interest in this paper, the properties of seawater vary with temperature T and salinity S in a smooth, continuous, and decreasing or increasing form and they have all the characteristics of "mathematically favorable" functions. Thus, these properties can be represented by polynomials and most probably by Padé expression with just few parameters. In some cases, it may be necessary to transform the variables to get the continuous monotonous change. The vapor pressure of seawater, for instance, is a property that is better modeled if the variable is represented as $\mathrm{Ln}(p)$.

The extension of Padé approximants to multivariable functions (such as properties of seawater that depend on two variables) has been matter of extensive mathematical studies [23–25]. From the practical point of view, however, the extension is more or less straightforward and, according to one author, multivariate Padé approximation "is a natural generalization of the univariate Padé approximation" [23]. The application presented in this paper considers the simple extension of Padé, and the proposal and analysis of approximants that include only linear expressions for $Q_m(x)$ and $R_n(x)$ in Eq. (4).

2.3. Proposed models

After analyzing the models available in the literature for the properties of seawater presented in Table 1 and observing the form of the curves at several temperatures and salinities (such as those shown in Fig. 1), it seems that a simple Padé considering both variables in the polynomials $Q_m(T,S)$ and $R_n(T,S)$ would be good enough to represent all properties, independent of the mathematical complexity of the models presented in the literature (polynomial, rational, logarithmic, or potential-type equations). The proposed general Padé model includes a maximum of seven parameters, but for some properties less than the seven parameters will be required. The Padé model is:

$$f(T,S) = \frac{a_1 + a_2 \times T + a_3 \times S + a_4 \times T \times S}{1 + b_2 \times T + b_3 \times S + b_4 \times T \times S} \tag{7}$$

If f_o is the function $f(T,S)$ evaluated at the reference point (T_o, S_o), and if the subindex "o" for each of the derivatives indicating that it corresponds to the derivative evaluated at (T_o, S_o), the series expansion of the function of two variables, T in kelvin, and S in (g of salt per kg of solution) is [26]:

$$\begin{aligned} f_n(T,S) = f_o &+ \left[\left.\frac{\partial f}{\partial T}\right|_o (T-T_o) + \left.\frac{\partial f}{\partial S}\right|_o (S-S_o)\right] \\ &+ \frac{1}{2}\left[\left.\frac{\partial^2 f}{\partial T^2}\right|_o (T-T_o)^2 + 2\left.\frac{\partial^2 f}{\partial T \partial S}\right|_o (T-T_o)(S-S_o) \right. \\ &\left. + \left.\frac{\partial^2 f}{\partial S^2}\right|_o (S-S_o)^2\right] + \frac{1}{6}\left[\left.\frac{\partial^3 f}{\partial T^3}\right|_o (T-T_o)^3 \right. \\ &+ 3\left.\frac{\partial^3 f}{\partial T^2 \partial S}\right|_o (T-T_o)^2 (S-S_o) \\ &\left. + 3\left.\frac{\partial^3 f}{\partial T \partial S^2}\right|_o (T-T_o)(S-S_o)^2 + \left.\frac{\partial^3 f}{\partial S^3}\right|_o (S-S_o)^3\right] \\ &+ Z_n(x) \end{aligned} \tag{8}$$

In the application presented in this study, $T_o = 273.15$ K and $S_o = 0$ (pure water) and the function $f(T,S)$ are the Padé expression (7).

What is interesting to analyze is how many terms in the series expansion (8) would be necessary to obtain the same value of $f(T,S)$ than that provided by the simple Padé of Eq. (7), in the whole range of the variables T and S. Literature information indicates that a simple Padé expression, such as the one described by Eq. (4) can represent a series of several terms. Not only that, but it is expected that the final Padé for the different properties can be simpler than the Padé of Eq. (7). For those properties that vary in a regular and monotonous way with both T and S, such as the osmotic coefficient or the thermal conductivity shown in Fig. 1, fewer parameters will certainly be needed. All these will be demonstrated in the next section.

Since the model includes two independent variables (T and S), the Padé will be named according to the number of parameters in the nominator and denominator of the Padé expression, and not according to the degree of the polynomial, as usually done when there is only one independent variable. Therefore, expression (7), for instance, is a $P_{4,3}$ model in the context of this work; four parameters in the numerator (a_1, a_2, a_3, a_4) and three parameters in the denominator (b_2, b_3, b_4).

The property $f(T,S)$ in Eq. (7) is any of the properties of seawater of interest in this work: density, specific heat, osmotic coefficient, viscosity, thermal conductivity, surface tension, enthalpy, entropy, vapor pressure, latent heat of vaporization, and boiling temperature elevation. Values of these properties are directly used to evaluate the Padé coefficients except for the vapor pressure, $y = p^{\text{vap}}$. For this property, the variation of p^{vap} with temperature is dramatic, going from approximately 1–200 kPa. This means that the ratio between the highest value of a property and the lowest value is of the order of 200. For the other properties, this ratio is smaller (from 2 to 20, depending on the property). Therefore, for the vapor pressure, the variable to be represented by Padé was the logarithm of the vapor pressure, $y = \text{Ln}(p^{\text{vap}})$. After changing the variable, the ratio between the highest and the lowest value of $\text{Ln}(p^{\text{vap}})$ is reduced to 25 (instead of 200 as using p^{vap} values). Once the Padé parameters are obtained, the vapor pressure is calculated ($p^{\text{vap}} = e^{y}$) and deviations between Padé and literature values are determined using vapor pressure values, p^{vap}, not the logarithm, $\text{Ln}(p^{\text{vap}})$.

2.4. Data and software used

Of the several models for estimating properties of seawater discussed by Sharqawy et al. [5], the most accurate expressions were used to generate pseudo-experimental values within the ranges of temperature and salinity indicated by the authors for each model and each property. The chosen models are those that according to Sharqawy et al. [5] give deviations below 1%, a value which is within experimental errors [5]. Table 2 specifies the equations used for generating the data used in the present study. The tables and equations referred to the paper by Sharqawy et al. [5]. The ranges of temperature and salinity are presented in Table 3. The different temperature and salinity scales considered by the different models presented in Table 1 for each of the properties have been standardized, and all Padé models presented in this work use absolute temperature in kelvin and salinity in grams of salt per kilogram of water.

Differences between values of temperature defined by the different scales are within the limits of accuracy of most common temperature measurement devices and certainly these differences have no practical influence within the ranges of temperature present in industrial processes [27,28]. For salinity, however, very different values for the same solution are found using the different salinity scales. The correlations mentioned in Table 1 for the several properties studied include Knudsen salinity (S_k), Chlorinity (Cl), and the Practical Salinity Scale (S_P). The reference-composition salinity S defined by Millero et al. [29] is currently the best estimate for the absolute salinity according to the International Association for the Physical Sciences of the Oceans (IAPSO) [5]. This salinity is designated by S and is the one used in the models proposed in this work. The relations between the different salinity scales are provided in Table 4.

There are several software packages capable of performing the type of optimization required in this

Table 2
Models used for generating the data used for each property

Property	Page	Table	Equation
Density	357	2	5
Vapor pressure	368	7	31
Boiling temperature elevation	368	7	35
Osmotic coefficient	375	10	49
Viscosity	364	5	16, 17, 23
Thermal conductivity	362	4	13
Surface tension	366	6	27, 28
Specific heat	360	3	9
Entropy	373	9	46
Enthalpy	371	8	43
Latent heat of vaporization	370	–	37
Pure water			
Vapor pressure	377	11	53
Entropy	378	11	56
Enthalpy	378	11	55
Latent heat of vaporization	377	11	54

Source: The page, the number of table, and the equation are those of the paper by Sharqawy et al. [5].

Table 3
Ranges of temperature ΔT and salinity ΔS for the development of the Padé models

Property	ΔT (K) (lit)	ΔT (K) (used)	ΔS (g/kg)	No. of data
Density	293–453	293–393	10–160	234
Vapor pressure	283–453	283–393	35–170	261
Boiling temp. elevation	293–453	293–393	35–100	130
Osmotic coefficient	273–473	273–393	10–120	217
Viscosity	293–423	293–393	15–130	208
Conductivity	273–453	273–393	0–160	279
Surface tension	273–313	273–313	0–40	205
Specific heat	273–453	273–393	0–180	310
Entropy	283–393	283–393	0–120	203
Enthalpy	283–393	283–393	0–120	203
Heat of vaporization	273–473	273–393	0–120	217

Table 4
Relations between the different salinity scales

$S = 1.00557 * S_k - 0.03016$
$S = 1.815068\ \mathrm{Cl}$
$S = 1.00472\ S_p$
$S_k = 0.99446\ S + 0.02999$
$\mathrm{Cl} = 0.55094\ S$
$S_p = 0.9953\ S$

work for determining the parameters of the Padé models. The software DataFit is the tool used in this work to perform nonlinear regression analysis and data plotting of multivariable functions and has the flexibility and accuracy required for this work. DataFit is an easy-to-use mathematical tool controlled by an intuitive graphics interface with clear instructions and menus. Data entry can be done through a standard spreadsheet interface or you can cut and paste data from the clipboard. DataFit performs linear and nonlinear regression of data containing up to 20 independent variables and it has many pre-defined equations, but one can also propose a new model if needed [30]. For the Taylor series expansion Matlab™ software was employed. The Padé expression was introduced in a Matlab code that transform the expression in a Taylor series.

3. Results and discussion

The accuracy of the models was analyzed by determining three statistical parameters that according to literature studies are the most appropriate for deciding about the goodness and accuracy of a mathematical model for a property "y" [6]: the average deviation ($\%\Delta y$), the average absolute deviation ($|\%\Delta y|$), and the maximum absolute deviation ($|\%\Delta y|_{\max}$):

$$\%\Delta y = \frac{100}{N}\sum_{1}^{N}\left[\frac{y_i^{\mathrm{cal}} - y_i^{\mathrm{lit}}}{y_i^{\mathrm{lit}}}\right] \tag{9}$$

$$|\%\Delta y| = \frac{100}{N}\sum_{1}^{N}\left|\frac{y_i^{\mathrm{cal}} - y_i^{\mathrm{lit}}}{y_i^{\mathrm{lit}}}\right| \tag{10}$$

$$\max\left|\%\Delta y_i\right| = 100\cdot\left|\frac{y_i^{\mathrm{cal}} - y_i^{\mathrm{lit}}}{y_i^{\mathrm{lit}}}\right| \tag{11}$$

The average deviation $\%\Delta y$ indicates how correlated values are dispersed around the experimental data. If deviations are well distributed with negative and positive values, the average deviation will be close to zero, independent of the magnitude of the deviations, because negative and positive deviations would cancel each other. The average absolute deviation $|\%\Delta y|$ gives an indication on how big are deviations. If these are low, the average would be low and most probably an acceptable model has been found. However, the maximum absolute deviation $|\%\Delta y|_{\max}$ is also important to observe because not only it highlights the value of this maximum during correlation, but it also gives an indication of the maximum deviation to be expected when the model is used for predicting a value for a given property.

3.1. Padé results

The values of the parameters in Eq. (7) for each of the properties were determined using the DataFit software and are shown in Tables 5–7. The optimum values of the parameters are those that produce the lowest average absolute deviations between correlated and literature values for the property studied. For

Table 5
Parameters of Padé model for physicochemical properties of seawater

	ρ (kg/m^3)		C (kJ/kg K)		p^{vap} (kPa)		BTE (K)	
Deviations and parameters	$P_{4,2}$	$P_{3,1}$	$P_{4,2}$	$P_{3,1}$	$P_{4,3}$	$P_{4,1}$	$P_{4,3}$	$P_{4,2}$
$\%y$	−0.01	0.02	0.01	0.01	−0.03	−0.04	<0.01	−0.01
$\lvert\%y\rvert$	0.03	0.13	0.14	0.41	0.07	0.10	0.07	0.10
$\lvert\%y\rvert_{max}$	0.12	0.52	0.83	1.74	1.49	2.06	0.34	0.57
a_1	1.007E + 03	1.015E + 03	4.172E + 00	4.134E + 00	−4.541E-01	−4.483E-01	−1.517E-02	−2.363E-02
a_2	−3.178E + 00	−8.485E-01	2.171E-02	1.711E-03	7.150E-02	7.152E-02	−4.707E-06	1.039E-04
a_3	6.435E-01	7.316E-01	3.466E-03	−4.053E-03	−3.159E-05	−6.580E-04	6.562E-03	6.768E-03
a_4	−2.179E-03		−1.656E-05		−7.900E-05	−2.831E-06	8.066E-05	8.057E-05
b_2	−2.811E-03	−2.848E-04	5.042E-03	2.665E-04	4.303E-03	4.303E-03	−2.304E-04	−4.056E-05
b_3	−9.931E-05		2.212E-03		−1.074E-03		−1.909E-03	−1.757E-03
b_4					−4.620E-06		2.198E-06	

Table 6
Parameters of Padé model for transport properties of seawater

	μ *10^3 (kg/m s)		k (mW/m K)		Ω		τ (mN/m)	
Deviations and parameters	$P_{4,3}$	$P_{4,1}$	$P_{4,3}$	$P_{3,1}$	$P_{4,3}$	$P_{4,1}$	$P_{4,3}$	$P_{3,1}$
$\%y$	−0.03	−0.05	0.01	−0.01	−0.03	0.04	−0.01	−0.01
$\lvert\%y\rvert$	0.47	0.82	0.18	0.18	0.68	1.14	0.01	0.03
$\lvert\%y\rvert_{max}$	2.36	2.38	0.50	0.55	2.49	3.74	0.03	0.07
a_1	1.953E + 00	1.911E + 00	5.692E + 02	5.700E + 02	8.937E-01	8.829E-01	7.562E + 01	7.567E + 01
a_2	−4.302E-03	−4.182E-03	8.068E + 00	7.812E + 00	1.959E-01	2.027E-01	−2.278E-01	−2.268E-01
a_3	−4.019E-04	5.960E-03	1.354E-02	−6.703E-02	−4.123E-03	7.073E-04	1.007E + 00	1.403E-02
a_4	2.489E-06	−1.141E-05	−1.990E-03		−9.520E-04	2.278E-04	−2.979E-03	
b_2	4.325E-02	4.360E-02	1.037E-02	1.001E-02	2.205E-01	2.322E-01	3.447E-04	3.753E-04
b_3	−2.326E-03		1.261E-04		−4.939E-03		1.302E-02	
b_4	−9.715E-05		−2.964E-06		−1.162E-03		5.347E-06	

each property, results for the two Padé expressions that give the lowest absolute average deviations are provided in the tables for comparison and discussion. Important to notice is that, depending on the accuracy needed, the simplest expressions can be adopted in engineering application without altering the results and their consequences. This is the case of the thermal conductivity, for instance, for which, $P_{4,3}$ and $P_{3,1}$ models give the same average absolute deviation (see Table 6), differing in the maximum deviation, which in any case is low and acceptable (0.50 and 0.55%, respectively). Thus, the $P_{3,1}$ model would be acceptable for process design and simulation of industrial processes.

As seen in Tables 5–7, the density, the thermal conductivity, and the surface tension were well correlated using a $P_{3,1}$ model, with three parameters in the numerator and one parameter in the denominator. For these properties, the average deviations is lower than or equal to 0.02%, the absolute average deviations is lower than 0.2%, and maximum deviations lower than 0.6%. The specific heat was well correlated using a simple $P_{3,1}$ model, with three parameters in the numerator and the one parameter in the denominator. For this property, the average deviation is 0.01%, the absolute average deviation is 0.41%, and the maximum deviation is 1.74%. Other properties require more complex expressions such as $P_{4,1}$ for the vapor pressure and the osmotic coefficient and $P_{4,2}$ for the boiling temperature elevation, the entropy, and the enthalpy. These latter results are expected if one considers the more complex dependency of these properties with temperature and salinity.

Important to mention is that the values of the parameters shown in Tables 5–7 are all presented with four significant figures and all results shown in those tables considered these values. We also checked that having more significant figures do not produce changes in the final value of a property nor in the deviations calculated for each model.

3.2. Taylor series calculations

To check the alleged superiority of Padé approximants over series expansions, the different properties were estimated by the Taylor series with increasing number of terms. Three cases using *Taylor series* were analyzed: *(1) with linear terms; (2) with linear and quadratic terms, and (3) Taylor series with linear, quadratic, and cubic term.* The Taylor series for $f(T,S)$ is:

$$\begin{aligned} f_3(T,S) = f_o &+ [(a_2 - b_2a_1)(T - T_o) + (a_3 - b_3a_1)(S - S_o)] \\ &+ \frac{1}{2}\left[(2a_1b_2^2 - 2a_2b_2)(T - T_o)^2 + 2(a_4 - a_2b_3 - a_3b_2 - a_1b_4 + 2a_1b_2b_3)(T - T_o)(S - S_o) + (2a_1b_3^2 - 2a_3b_3)(S - S_o)^2\right] \\ &+ \frac{1}{6}\left[(-6a_1b_2^3 + 6a_2b_2^2)(T - T_o)^3 + 3(-2a_4b_2 + 4a_2b_2b_3 - 2a_2b_4 + 2a_3b_2^2 + 4a_1b_2b_4 - 6a_1b_2^2b_3)(T - T_o)(S - S_o)^2\right] \\ &+ \frac{1}{6}\left[3(-2a_4b_3 + 4a_3b_3b_2 - 2a_3b_4 + 2a_2b_3^2 + 4a_1b_3b_4 - 6a_1b_3^2b_2)(T - T_o)^2(S - S_o) + (-6a_1b_3^3 + 6a_3b_3^2)(S - S_o)^3\right] \end{aligned} \tag{12}$$

These three Taylor series expansions were analyzed and values of $f(T,S)$ calculated for different values of temperature T and salinity S. In Table 8, comparison of the accuracy provided by the various complex models listed by Sharqawy et al. [5] and the result of the Taylor series (with linear, quadratic, and cubic terms) and the simplest Padé models presented in this paper are shown. To be fair when comparing the results of Padé and those mentioned in Table 1, the following considerations were taken into account: (1) the literature models in Table 1 that include the pressure as an independent variable were not considered (those marked with the symbol * in the second column of Table 1); (2) the models valid in ranges different from those used in applying Padé were not considered; (3) if more than one literature model is comparable, comparison is done with the literature model that gives the lowest deviation and having the lower number of parameters.

As seen in Table 8, in most cases, deviations provided by Padé are lower than those of more sophisticated models having usually greater number of parameters and of Taylor series expansions including up to third-order terms (T^3, S^3, T^2S, TS^2). Remarkable is the case of osmotic coefficient in which a $P_{4,1}$ (five parameters) gave lower deviations than polynomials or potential functions having 10 parameters. Thermal conductivity was well modeled with a $P_{3,1}$ model (containing four parameters and with average deviation of −0.01%), while a complex potential-rational-logarithmic expression including nine parameters has been reported to give average deviations of 3% [5].

Table 7
Parameters of Padé model for thermodynamic properties of seawater

	Ψ (kJ/kg K)		h (kJ/kg)		Δh^{vap} (kJ/kg)	
Deviations and parameters	$P_{4,3}$	$P_{4,2}$	$P_{4,3}$	$P_{4,2}$	$P_{4,2}$	$P_{3,1}$
$\%y$	−0.01	−0.05	−0.04	−0.02	−0.02	0.01
$\lvert\%y\rvert$	0.42	0.42	0.23	0.26	0.02	0.13
$\lvert\%y\rvert_{max}$	6.39	6.59	3.15	2.70	0.05	0.59
a_1	1.186E-02	1.244E-02	1.644E + 00	−1.262E-01	2.500E + 03	2.501E + 03
a_2	1.490E-02	1.487E-02	4.127E + 00	4.202E + 00	−3.948E + 00	−1.507E + 00
a_3	−4.709E-04	−4.797E-04	−6.162E-02	−3.182E-02	−2.500E + 00	−2.412E + 00
a_4	−3.864E-05	−3.829E-05	−4.065E-03	−4.495E-03	3.948E-03	
b_2	1.498E-03	1.482E-03	−1.107E-04	2.758E-05	−6.690E-04	3.932E-04
b_3	−1.941E-03	−1.945E-03	−1.538E-04	7.274E-05	8.055E-10	
b_4	−2.545E-07		2.456E-06			

Table 8
Comparison of accuracy between literature correlations and this work. The cells show the absolute % deviation $\lvert\%\Delta y\rvert$, the number of parameters (par), and model type (Lin = linear, Pol = polynomial, Log = logarithmic, Rat = rational, and Pot = potential)

Property	Various models (Sharqawy et al. [5])	Taylor series $f_1(T,S)$	Taylor series $f_2(T,S)$	Taylor series $f_3(T,S)$	Padé (this work)
Density	0.1% (Pol; 10 par)	0.15	0.14	0.14	0.13 ($P_{3,1}$; 4 par)
Vapor pressure	0.07% (Log; 8 par)	33.35	10.93	13.59	0.10 ($P_{4,1}$; 5 par)
Boiling temperature elevation	0.7% (Pot; 6 par)	50.96	8.72	6.39	0.10 ($P_{4,2}$; 6 par)
Osmotic coefficient	1.4% (Pot; 10 par)	15.52	150.47	1,085.41	1.14 ($P_{4,1}$; 5 par)
Viscosity	0.4% (Rat + Pot + Log; 12 par)	1,128.13	1,583.86	2,074.18	0.82 ($P_{4,1}$; 5 par)
Thermal conductivity	3% (Rat + Pot + Log; 9 par)	7.99	0.92	2.90	0.18 ($P_{3,1}$; 4 par)
Surface tension	0.1% (Lin; 4 par)	0.09	0.05	0.05	0.03 ($P_{3,1}$; 4 par)
Specific heat	0.28% (Pol; 12 par)	0.42	0.41	0.41	0.41 ($P_{3,1}$; 4 par)
Entropy	0.5% (Pol; 15 par)	18.01	7.10	6.45	0.42 ($P_{4,2}$; 6 par)
Enthalpy	0.5% (Pol; 14 par)	7.88	0.28	0.28	0.26 ($P_{4,2}$; 6 par)
Latent heat of vaporization	0.01% (Pol; 5 par)	0.42	0.17	0.17	0.13 ($P_{3,1}$; 4 par)

The case of surface tension is interesting, since the models proposed in the literature are linear in T and S (with four parameters). This occurs because the ranges of temperature and salinity for the surface tension are much narrower than for the other properties, as shown in Table 3. Although the linear model is simpler than any Padé expression, the latter has the advantage of keeping accuracy in case, the ranges of temperature and salinity are wider. The parameters of the proposed Padé should be re-calculated if more data are available.

4. Conclusions

According to the results and the analysis presented in this paper, the following main conclusions can be drawn: (1) the proposed Padé model showed to be successful for correlating the properties of seawater studied in this paper; (2) just one type of model allows correlating all properties of seawater; and (3) the sophisticated equations commonly presented in the literature for estimating properties of seawater are not necessary for process design in which seawater is employed.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.10.1080/19443994.2015.1022806.

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Symbols

a_i, b_i, c_i, d_i — coefficients in Padé and other correlations
Cl — chlorinity
C — specific heat
e — Euler's number
$f(x)$ — general function of x
f_0 — general function $f(x)$ evaluated in $x = 0$
$f(T,S)$ — property, function of temperature, and salinity
$f_n(T,S)$ — Taylor expansion of order n
g — gram
h — enthalpy
k — thermal conductivity
K — kelvin
kJ — kilojoule
kg — kilogram
kPa — kilopascal
m — meter
m^3 — cubic meter
m, n — degree of the numerator and denominator in Padé
mW — mili watt
mN — mili newton
N — newton
p — pressure
p^{vap} — vapor pressure
$P_{m,n}(x)$ — general Padé model
q_m, r_n — coefficients in Padé
$Q_m(x), R_n(x)$ — polynomials in Padé
s — second
S — salinity
S_0 — zero salinity (pure water)
S_k — Knudsen salinity
S_P — practical Salinity
t — temperature (°C)
t_{27} — temperature scale 1927 (°C)
t_{48} — temperature scale 1948 (°C)
t_{68} — temperature scale 1968 (°C)
T_0 — absolute reference temperature (273.15 K)
T — absolute temperature (K)
T_{48} — absolute temperature scale 1948 (K)
W — watt
x — general variable
x_0 — reference value for x
% — percentage
$^0/_{00}$ — parts per thousand
$\%\Delta y$ — average deviation of property y
$|\%\Delta y|$ — average absolute deviation of property y
$_{\max}|\%\Delta y|$ — maximum absolute deviation of property y
y^{cal} — calculated property
y^{lit} — literature property

Abbreviations

BTE — boiling temperature elevation
Eq. — equation
Lin — linear
Ln — natural logarithm
Log — logarithmic
Par — parameter
Pol — polynomial
Pot — potential
Rat — rational

Greek letters

α, β, γ — coefficient of Padé
α_i — coefficient in general function $f(x)$
$\frac{\partial x}{\partial y}$ — partial derivative of "x" with respect to "y"
Δ — difference
$\%\Delta$ — percent deviation
Δh^{vap} — heat of vaporization
Σ — summation
ρ — density
μ — viscosity
η — number of points in a data-set
τ — surface tension
Ω — osmotic coefficient
Ψ — entropy

Super/subscripts

cal — calculated
lit — literature
max — maximum
m — degree of polynomial in Padé numerator
n — degree of polynomials in Padé denominator

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