The electrical conductivity of seawater at high temperatures and salinities

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ABSTRACT

Recently a new international standard for the thermodynamic properties of seawater, the Thermodynamical Equation of Seawater—2010 (TEOS-10), has been developed. For some properties it is valid at the high temperatures and salinities that may be found in industrial and desalination processes. However, precise in situ estimates of mass fraction salinities, derived from measurements of electrical conductivity in TEOS-10 using a modification of the Practical Salinity Scale 1978 (PSS-78), have been validated only when temperatures are less than 35 °C and salinities are less than 42 g/kg. The algorithm has not been validated at higher temperatures and salinities. Here a combination of numerical modeling and measurements is used to determine the electrical conductivity of high salinity and high temperature seawater. It is found that the TEOS-10 salinity algorithm can be used without other corrections to estimate seawater salinities from electrical conductivity for all temperatures between freezing and boiling and all salinities up to the point of calcite precipitation with an accuracy of 1% to 2% or better.

1. Introduction

Recently a new standard for all of the thermodynamical properties of seawater has been endorsed by a number of international organizations including the International Association for the Properties of Water and Steam (IAPWS), the Intergovernmental Oceanographic Commission (IOC), the International Union of Geodesy and Geophysics (IUGG), the International Association for the Physical Sciences of the Ocean (IAPSO), and the Scientific Committee on Oceanographic Research (SCOR). This new standard, the Thermodynamical Equation of Seawater 2010 (TEOS-10) [1], is formulated as a Gibbs function for seawater from which all thermodynamical properties including density, sound speed, heat capacity, enthalpy, entropy, and others can be derived in a manner consistent with laws of thermodynamics. Property variations with salinity are parameterized using the new Reference Composition Salinity Scale. Salinities on this scale are referred to as Absolute Salinities, denoted S_A, and represent the best estimate of the mass fraction of dissolved inorganic material in seawater.

For some thermodynamic properties TEOS-10 is valid for Absolute Salinities of 0 to 120 g/kg (or until precipitation of $CaCO_3$ occurs), and temperatures from the freezing point to 80 °C. Density estimates are valid only for Absolute Salinities up to 50 g/kg, but a recently proposed extension provides precise density estimates for temperatures up to 90 °C and Absolute Salinities up to 70 g/kg [2], based on new measurements of densities under these conditions [3].

In order to determine these thermodynamic properties, and/or in order to quantify the mass fraction of dissolved matter in a particular

sample of seawater, it is therefore necessary to determine the Absolute Salinity. Since the ionic content of seawater controls its electrical conductivity, measurements of the latter are widely used as a proxy for this purpose. Electrical conductivity can be measured relatively easily, either in the laboratory or in situ. In the oceanic or "Neptunian" range of seawater conditions (temperatures of −2 to 35 °C and salinities of 2 to 42 g/kg) precise estimates of the Absolute Salinity under TEOS-10 can be obtained from in-situ measurements of electrical conductivity and temperature using a modification of the Practical Salinity Scale 1978 (PSS-78) [4]. However, at present there is no standard way of making in situ measurements of the salinity of seawater outside the Neptunian range, e.g., at the high temperatures that may occur in industrial processes, or at the high salinities that can occur during desalination. This is because the relationship between electrical conductivity and Absolute Salinity is not known under such conditions.

In these high salinity and/or high temperature situations, water samples can instead be analyzed by reducing their temperature, and/or by diluting with pure water until their salinities are in the measurable range for PSS-78 or for a measurement of density (from which salinity can be found by inverting the TEOS-10 density equation) but the necessity of manipulating samples is often inconvenient. Specialized calibrations for in-situ measurements in specific situations can be carried out by comparison with samples of "known" salinity, but this requires the production of high-salinity standards. Finally, measured in-situ conductivities can always be "converted" into salinities by blindly applying the existing mathematical algorithms specified by TEOS-10/PSS-78, but this assumes that such extrapolations into high salinity and high temperature conditions are valid. These assumptions have never been tested.

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In this paper the latter technique is considered. The accuracy of the TEOS-10 modification of PSS-78 is evaluated when its use is extrapolated into high temperatures and salinities, at atmospheric pressure. Estimates of seawater conductivity in these extreme conditions will be made using a numerical model for predicting the electrical conductivity of multi-component aqueous solutions [5], bias-corrected using measurements of NaCl solutions at the same salinities. Although it had been expected that an additive correction to PSS-78 could improve accuracies, as is the case for low-salinity waters [6], the calculations presented here suggest that TEOS-10/PSS-78 can be used without modification to make salinity estimates with an accuracy of ± 1% to 2% over the whole range between the freezing and boiling points of seawater, and for salinities up to the point at which precipitates form. These limitations on accuracy are determined primarily by the quality of the NaCl measurements, although it is unlikely that more precise measurements would decrease this bound by more than an order of magnitude. Although the stated accuracy is significantly lower than the level required for specialized oceanographic research studies in the deep ocean ($\approx \pm 0.006\%$ [7]), it is comparable to the accuracy of many commercially available conductivity meters and hence is sufficient for many engineering and industrial processes where these high salinities and temperatures may occur.

2. Methods

2.1. TEOS-10, Absolute Salinity, and electrical conductivity

Although the term salinity is generally associated with a measure of inorganic solute mass fraction in a natural water, any precise, reproducible, and practically useful definition of salinity inevitably incorporates a number of compromises and idealizations. Under TEOS-10 the salinity variable is named the Absolute Salinity and represents the mass fraction of inorganic solute on the Reference Composition Salinity Scale [1]. This scale is exact for a seawater whose chemical composition is described by the Reference Composition [8].

Reference Composition includes all constituents that normally occur in amounts of about 0.001 g/kg or greater in typical low-nutrient seawater with $S_A \approx 35$ g/kg, with the exception of dissolved gases O_2 and N_2, which are generally present in concentrations of 0 to 0.010 g/kg and 0.014 g/kg respectively, but which have little effect on density or electrical conductivity. In addition, all important components of the carbonate system are included, including several (e.g., dissolved CO_2 gas) which do not meet the 0.001 g/kg threshold but which are important in determining chemical equilibria [9].

For Reference Composition Seawater, the mass fraction of solute is denoted the Solution Salinity S_A^{soln}, which can be loosely defined as the sum of the masses of all constituents in solution:

$$S_A^{soln}/(g/kg) \equiv \sum_{i=1}^{N} c_i M_i \qquad (1)$$

where the ith of N constituents has a known concentration $c_i/(mol/kg)$ and molar mass $M_i/(g/mol)$ [8]. Formally, S_A is defined to be S_A^{soln} for Reference Composition Seawater.

Note that the actual definition of the Reference Composition Scale is slightly more complex since Eq. (1) does not account for temperature and concentration-dependence of chemical equilibria in the carbonate system. The precise definition compensates for these variations by adding or removing pure water until the measured electrical conductivity at a specified reference temperature and pressure is fixed at a specified value, calculating the sum (1), and then correcting by the dilution factor. This manipulation results in relative numerical differences of as large as 0.001% relative to a naive calculation of Eq. (1). Equilibration with atmospheric levels of $CO_{2(g)}$ during the

manipulation (e.g., by stirring open containers during evaporation or dilution) results in further relative differences of as large as 0.05% for salinities near 70 g/kg [10]. These are important distinctions for deepwater oceanographic studies but will be ignored here.

However, the best practical method for determining the Absolute Salinity does not involve Eq. (1) directly. Instead one either finds the Density Salinity S_A^{dens} directly through measurements of density $\hat{\rho}$ at a specified temperature t_{90} and pressure p, and inversion of the TEOS-10 density equation:

$$S_A^{dens} \, defined \, such \, that \, \hat{\rho} = \rho_{TEOS-10}\left(S_A^{dens}, t_{90}, p\right) \qquad (2)$$

or, in the "Neptunian" range of seawater conditions (temperatures of − 2 to 35 °C and Absolute Salinities of 2 to 42 g/kg) one measures the electrical conductivity to estimate a Reference Salinity S_R:

$$S_R/(g/kg) \equiv u_{PS} \times S_P(R, t_{68}, p) \qquad (3)$$

where S_P is the traditional Practical Salinity defined by the Practical Salinity Scale 1978 [4], and the factor $u_{PS}/(g/kg) \equiv 35.16504/35$ scales the results to give the correct value for Reference Composition seawater [8]. This correction is necessary because the PSS-78 was defined before the chemical composition of seawater had been accurately determined.

For Reference Composition seawater $S_A^{soln} = S_A^{dens} = S_R$ by design [8]. However, for real seawaters, whose relative chemical composition can vary from that of Reference Composition seawater, they may be numerically different. This is because different constituents have different contributions to conductivity and density for a given mass. The numerical differences can be as large as 0.03 g/kg (a relative change of 0.1% for typical seawater with $S_A \approx 35$ g/kg) in the open ocean and in coastal areas can be as large as 0.1 g/kg [11,12], and hence are important for oceanographic studies.

For real seawaters, S_A is formally defined to be S_A^{dens}, because density is the most widely required physical property of seawater [11]. Use of density as a measure of salinity is already common practice for brines [13], so the primary novelty here is the use of TEOS-10 algorithms and the Reference Composition Salinity Scale. However, since the largest numerical variation between the different salinity definitions, related to these changes in composition, is a relative change of only about 0.3% for typical seawater with $S_A \approx 35$ g/kg the effect is small relative to the other uncertainties in the analysis described in this paper, and the Reference Composition will be taken as a sufficiently accurate idealization of real seawater. Then, the only differences between S_R (from Eq. (3)) and S_A^{soln} arise because the use of PSS-78 algorithm for S_P does not completely remove pressure and temperature dependence.

The Practical Salinity defined by PSS-78 is calculated from in-situ observations using three measured variables: R, a nondimensional ratio of the conductivity κ of a water sample relative to the conductivity of a KCl solution with a carefully specified concentration at atmospheric pressure and a temperature of 15 °C on the IPTS-68 scale:

$$R = \frac{\kappa}{\kappa(KCl, 15, 0)} \qquad (4)$$

as well as t_{68}, the temperature on the IPTS-68 scale, and p the pressure in excess of atmospheric pressure at sea level. Temperatures on the IPTS-68 scale can be estimated from measurements t_{90} on the currently used ITS-90 scale [14] using the relationship [1]

$$t_{68}/(^{o}C) = 1.00024 \times t_{90}/(^{o}C) \qquad (5)$$

Precision laboratory salinometers traditionally do not return values of S_P or R for water samples, but rather a related quantity R_T. R_T is the nondimensional ratio of sample conductivity κ relative to

the conductivity κ_{SSW} of a reference material, IAPSO Standard Seawater with $S_P = 35$, at a known temperature:

$$R_T(t_{68}) = \frac{\kappa(S_P, t_{68})}{\kappa_{SSW}(t_{68})} \qquad (6)$$

where conversions between R and R_T are made using equations specified in PSS-78 to account for the temperature dependence of the conductivity of Standard Seawater.

IAPSO Standard Seawater is produced and distributed by a single source (Ocean Scientific International Ltd., UK) that maintains the reference KCl solution, and is a physical artifact realizing the Reference Composition. Standard Seawater is used as a reference in precision salinometry because the temperature dependence of the conductivity of all seawaters is similar, but rather different than that of KCl.

This elaborate procedure is used in oceanography instead of an absolute measurement of electrical conductivity because a measurement of conductivity traceable to the International System of Units (SI) is possible only to an accuracy of 0.03% [15], whereas open-ocean hydrographic measurements require a precision and intercomparability of about 0.006% [7]. However, at SI-traceable levels of accuracy a much simpler procedure can be used bypassing Standard Seawater, and the conductivity ratio R can be related to absolute measurements of conductivity κ using a scale factor:

$$\kappa/(\text{mS/cm}) = R \times 42.9140 \qquad (7)$$

[16] thus allowing the functional definition $S_P = S_P(\kappa, t_{90}, p)$ for Practical Salinity to be assumed in this paper. Dependence on p will also be dropped since the analysis will be carried out only at atmospheric pressure ($p = 0$). A similar simplification is used in many hand-held salinity meters, whose typical accuracy is of order 1%.

2.2. Conductivity modeling

Estimates of the electrical conductivity $\kappa_{SEAWATER}$ of seawater of known S_A, at arbitrary temperatures, will be made using the LIMCOND numerical conductivity model [5], which can calculate the electrical conductivity of an arbitrary aqueous solution containing a known composition of dissolved ions, at a specified temperature.

At salinities in the range of oceanic interest LIMCOND is affected by biases, so that a model estimate of conductivity $\kappa^{(m)}$ calculated from a specified composition $\{c_i, i = 1 \ldots N\}$ differs from the true conductivity $\kappa^{(d)}$ of such a solution by a bias factor $1 + \varepsilon$:

$$\kappa^{(d)} = \kappa^{(m)} \cdot (1 + \varepsilon)^{-1} \qquad (8)$$

The (d) superscript implies a measurement (i.e. data), and the (m) superscript a model calculation. For typical ocean water ε is found to be around -0.1 and decreases slowly with salinity, but is relatively insensitive to the changes in relative composition that characterize natural waters [10].

At this level of bias the model is not accurate enough to be used directly for the purposes of this paper. However, calculations can be adjusted for these biases by using the model to estimate only the small changes in conductivity that arise from small changes in composition, under conditions in which the bias is approximately constant. Such a procedure was previously used to investigate the nature of the differences between S_R and S_A that arise from biogeochemical processes in an oceanographic context [10,12].

Since the composition of seawater is dominated by NaCl, for which many measurements have been published, LIMCOND will therefore be used to find the differences in conductivity between an NaCl solution and a seawater solution containing the same mass fraction of dissolved material. The conductivity of NaCl solutions is on the order of 6% to 8% higher than that of seawater of the same S_A^{soln} in the Neptunian range so this is the size of the effect being modeled.

The model-derived perturbation will be bias-corrected, and then added to measured values of the electrical conductivity NaCl solutions at the same S_A^{soln} to provide complete estimates of seawater conductivity:

$$\kappa_{SEAWATER} = \kappa_{NaCl}^{(d)} + \left(\kappa_{SEAWATER}^{(d)} - \kappa_{NaCl}^{(d)} \right) \qquad (9)$$

$$\approx \kappa_{NaCl}^{(d)} + \left(\kappa_{SEAWATER}^{(m)} - \kappa_{NaCl}^{(m)} \right) \cdot (1 + \varepsilon)^{-1} \qquad (10)$$

$$= \kappa_{SEAWATER}^{(m)} \cdot \frac{\kappa_{NaCl}^{(d)}}{\kappa_{NaCl}^{(m)}} \qquad (11)$$

where the model bias for seawater, assumed to be the same as for an NaCl solution of the same Absolute Salinity, is estimated via Eq. (8) using model calculations and experimentally derived data for NaCl solutions.

A typical bias correction of order 10%, applied to a model-derived perturbation of order 8% will change $\kappa_{SEAWATER}$ estimates by less than 1%. Even if the bias itself has composition dependence of 10% $\pm$ 3%, the associated uncertainty in $\kappa_{SEAWATER}$ will be only $\pm$ 0.2%.

3. Experimental data

The utility of the modeling approach depends not only on the insensitivity of model bias to changes in relative composition as discussed in Section 2, but also on the quantity and quality of experimental data available for NaCl solutions, since errors in these measurements result in equivalent errors in the seawater conductivity estimates via Eq. (11). Many measurements of relatively dilute NaCl solutions have been made, with salinities comparable to those of river and lake waters, at temperatures between 0 °C and 50 °C. There are fewer measurements at higher concentrations and/or higher temperatures, but even so NaCl is relatively well-studied compared to many other salts (Fig. 1).

Since electrical conductivity has a strong dependence on concentration, it is conventional to discuss a related parameter, the equivalent conductivity Λ where

$$\Lambda = \frac{\kappa}{m} \qquad (12)$$

(Fig. 2) with m the molarity of solute. In the limit of infinite dilution, Λ varies with $\sqrt{m}$.

A comprehensive and high-precision dataset for NaCl solutions with concentrations from 0 to 200 g/kg was obtained by Chambers et al. [18], at 25 °C, with a stated uncertainty of 0.03% [17], and at 50 °C with an uncertainty of 0.07% (Fig. 1). A number of measurements at 0, 18, 25, 50 and 100 °C are compiled in the International Critical Tables [19], although the original sources are more than 80 years old. Their precision is not stated. Five relatively concentrated solutions were also measured at 10 °C intervals between 0 and 100 °C by Lyle and Hosking [20]. However, the concentrations of their solutions were determined only "approximately"; comparisons with other measurements (Fig. 2) suggest that the precision of the measurements is high, but that significant biases may occur at each concentration, possibly related to the uncertainty in concentration. Additional measurements at 100 °C have been made as part of a program of high-temperature and high-pressure measurements [21,22]. A complicating factor with older measurements is that the changes in the definitions of resistance, temperature, the liter, and atomic weights have changed the values of primary conductivity standards by up to 0.1%, and these changes are not always accounted for [23].
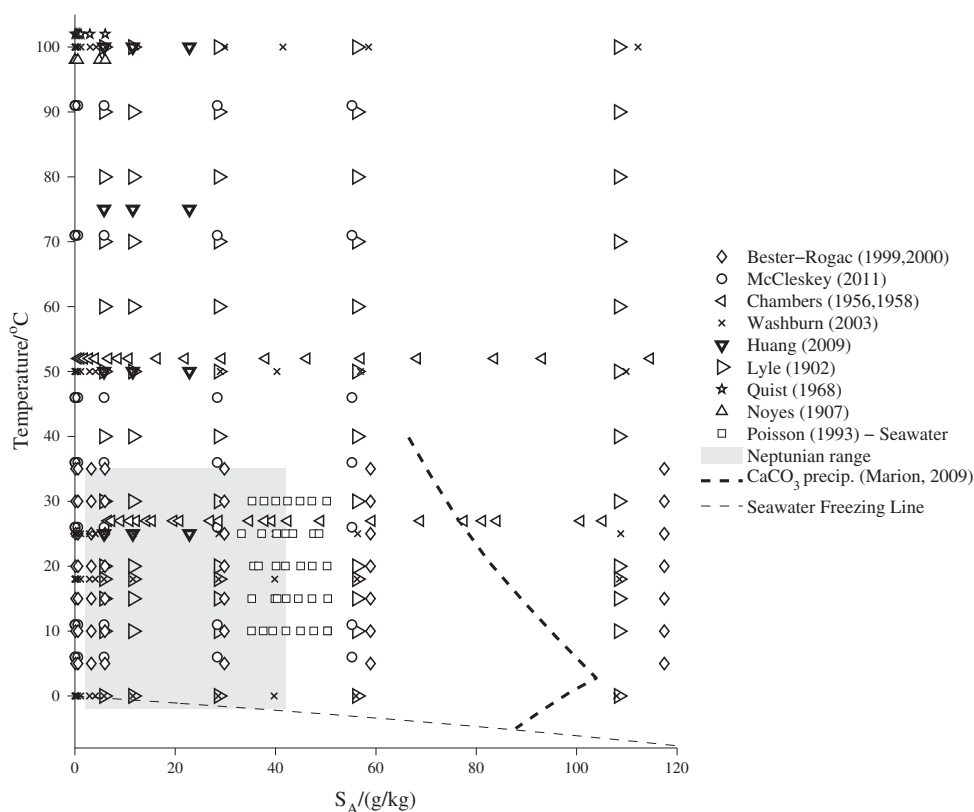
Fig. 1. Distribution of data (some datasets have been shifted vertically by 1 or 2 °C to make markers more visible). Shaded regions represents "Neptunian" conditions within which Eq. (3) is accurate to 0.006%. Also shown are bounding curves for the formation of water ice, and of evaporation-driven CaCO$_3$ precipitation for $t<40$ °C (from Fig. 2 of Marion et al. [30]).

More modern measurements of the conductivity of NaCl solutions include those of Bešter-Rogač et al. [24,25], over concentrations ranging from 0.001 to 3 mol/kg (i.e., absolute salinities of 0.06 to 175 g/kg),

at temperatures from 5 to 35 °C, with a stated uncertainty of ±0.2%. Measurements were also made by McCleskey [26] for concentrations ranging from 0.001 to 1 mol/kg (0.06 to 58 g/kg), at a number of
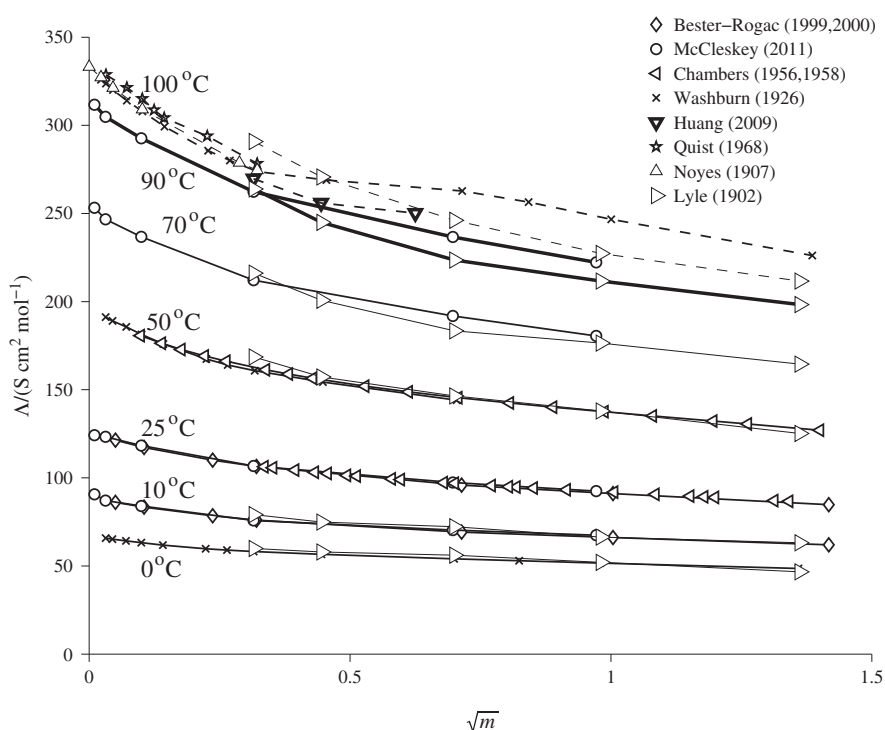

Fig. 2. Equivalent conductivities of aqueous **NaCl** solutions at selected temperatures, as measured by various workers. Values in a particular dataset at equal temperatures are joined by thin lines for temperatures less than 90 °C, by thick lines at 90 °C, and by dashed lines at 100 °C.

temperatures between 5 to 90 °C. Although a formal uncertainty was not stated, the scatter relative to smooth curve fits suggests that the uncertainty for their dataset as a whole is approximately 1.6%, with larger differences at higher temperatures and salinities. Lower-accuracy measurements were made at 25, 50, 75, and 100 °C by Huang and Papangelakis [27]. Although no uncertainty was stated, the temperature accuracy was ± 2 °C which suggests an uncertainty of at least $\pm 2\%$.

In general, although disagreements between different datasets are often slightly larger than the stated uncertainties imply, measurements at temperatures below 50 °C are relatively consistent at the 1% level. This may be due to the existence of a tabulated KCl conductivity standard for temperatures in this range. However, at higher temperatures disagreements are larger, and approach 10% at concentrations greater than 0.1 mol dm^{-3} for temperatures of 100 °C (Fig. 2), although the available data at lower concentrations for this temperature is relatively consistent. Extrapolating trends at lower temperatures suggests that the high-temperature measurements of McCleskey [26] and in the Critical Tables [19] may be biased upward.

In addition to these measurements of NaCl, direct measurements of the conductivity ratio R for evaporated and diluted seawater with Absolute Salinity in the range of 30 to 51 g/kg at temperatures of 10 to 30 °C (i.e. slightly outside the region of validity of PSS-78) were made by Poisson and Gadhoumi [28]. Although covering a limited set of temperatures and salinities, these measurements are of the highest accuracy, with an uncertainty on the order of 0.01%.

In many cases, comparisons require conversions between different concentration scales (e.g., between molarities and molalities and/or the reverse). Density of NaCl solutions at temperatures ≤ 50 °C is based on laboratory measurements of Lo Surdo et al. [29]. At higher temperatures values are interpolated from the Critical Tables [19]. Agreement between the two for temperatures ≤ 50 °C where they overlap is better than 0.03%.

4. Results

Modeled seawater conductivities, bias corrected by NaCl measurements, range over several orders of magnitude (Fig. 3). The calculated

values are in good visual agreement with the electrical conductivities that would be implied by the use of TEOS-10 via Eq. (3) not only in the Neptunian range but over the whole range considered.

More quantitatively, consider the relative error α between S_R determined from modeled conductivity $\kappa_{SEAWATER}$ through Eqs. (11), (7), and (3), applied without regard for the Neptunian range over which PSS-78 is formally valid, and $S_A = S_A^{soln}$:

$$\alpha(\kappa_{SEAWATER}, t) = \frac{S_A - S_R}{S_A} \tag{13}$$

First, consider α for Neptunian salinities at temperatures between 0 and 50 °C (Fig. 4). In this range, α estimates have a mean and standard deviation of -0.002 ± 0.009 and a root-mean-square (RMS) variation from zero of 0.009. Although the nonzero mean offset suggests that model biases may not have been perfectly corrected, the overall RMS scatter is consistent with the quality of the NaCl data and known model performance.

Highly precise measurements of seawater conductivity were made at salinities of up to 51 g/kg by Poisson and Gadhoumi [28] for a limited range of temperature (Fig. 1). Their data consist of triplets $\{R_T, S_W, t_{68}\}$ where S_W is a Practical Salinity measurement on a diluted version of the sample, rescaled by the dilution factor. Substitution of the conductivity measurements directly into the TEOS-10 algorithms can be compared with S_W to form another estimate of α_{PG} of relative error which is independent of any model calculations:

$$\alpha_{PG}(\kappa_{SEAWATER}, t) = \frac{u_{PS} S_W - u_{PS} S_P(R_T, t)}{u_{PS} S_W} \tag{14}$$

For salinities <42 g/kg α_{PG} should be zero. The RMS value is 0.0001, consistent with the accuracy of the measurements. At higher salinities α_{PG} is slightly negative (Fig. 4), but a fit finds that α_{PG} at 50 g/kg is only about -0.0003. Extrapolating this trend to 100 g/kg suggests a bias of order -0.002 at most. Although important in an oceanographic context, this bias is negligible relative to the scatter in the NaCl-based estimates.
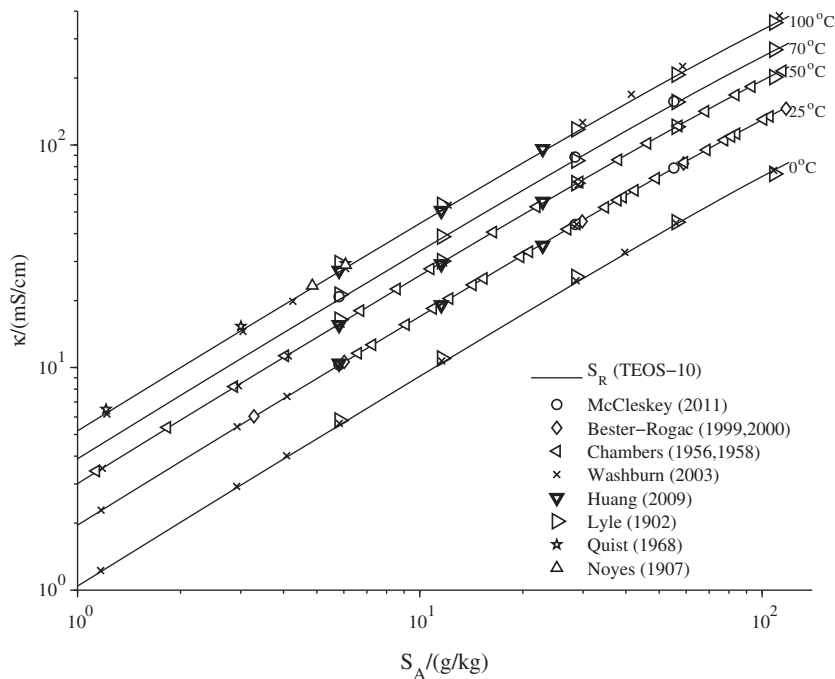

Fig. 3. Conductivity of seawater as a function of Absolute Salinity for selected temperatures. Curves show estimates obtained by inverting the TEOS-10 algorithm, with conductivity ratios R and conductivities κ related according to Eq. (7). Markers show numerical model estimates of seawater conductivities, bias-corrected using measurements of NaCl solutions made by different workers.
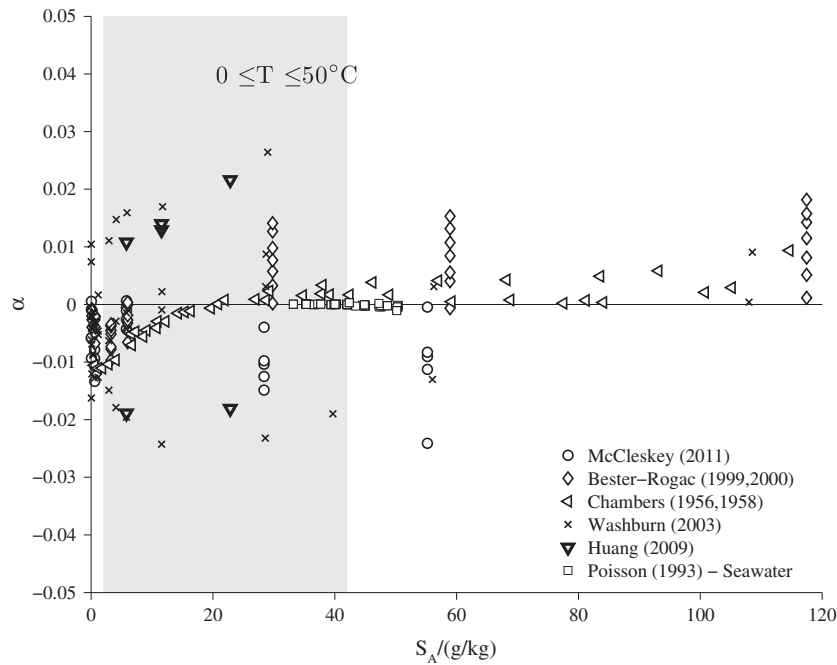
Fig. 4. Variations with salinity of relative error α between S_R determined from modeled conductivity $\kappa_{SEAWATER}$ through Eqs. (11), (7), and (3), applied without regard for the Neptunian range over which PSS-78 is formally valid, and $S_A = S_A^{soln}$, for temperatures $\leq 50\ ^\circ C$. Shaded region represents Neptunian salinities.

Linear extrapolation of the precise measurements [28] to higher salinities may not be valid. However, NaCl-based estimates of α at high salinities are also close to zero, albeit with a slight positive trend at salinities > 100 g/kg (Fig. 4). In spite of this possible trend, the RMS variation in α estimates at temperatures of 0 to 50 °C for salinities of 4 to 120 g/kg is only 0.01. This suggests that it is reasonable to assign an error of between 0.2% and 1% for all salinities estimated using TEOS-10/PSS-78, extrapolated without change, at temperatures less than 50 °C.

At temperatures greater than 50 °C the disagreement between different measurements of NaCl conductivities produces wider scatter (Fig. 5), but no consistent trend. The upward bias in measurements of Lyle and Hosking [20] at 0.1 mol dm^{-3}, and for the high-salinity measurements previously mentioned [19,26] result in larger negative values for α, but even including all these points the mean and standard deviation of α is only -0.007 ± 0.02 and the RMS variation 0.02.

In summary then, TEOS-10 can be used via Eq. (3) to estimate the Absolute Salinity of high-salinity seawater at temperatures <50 °C to
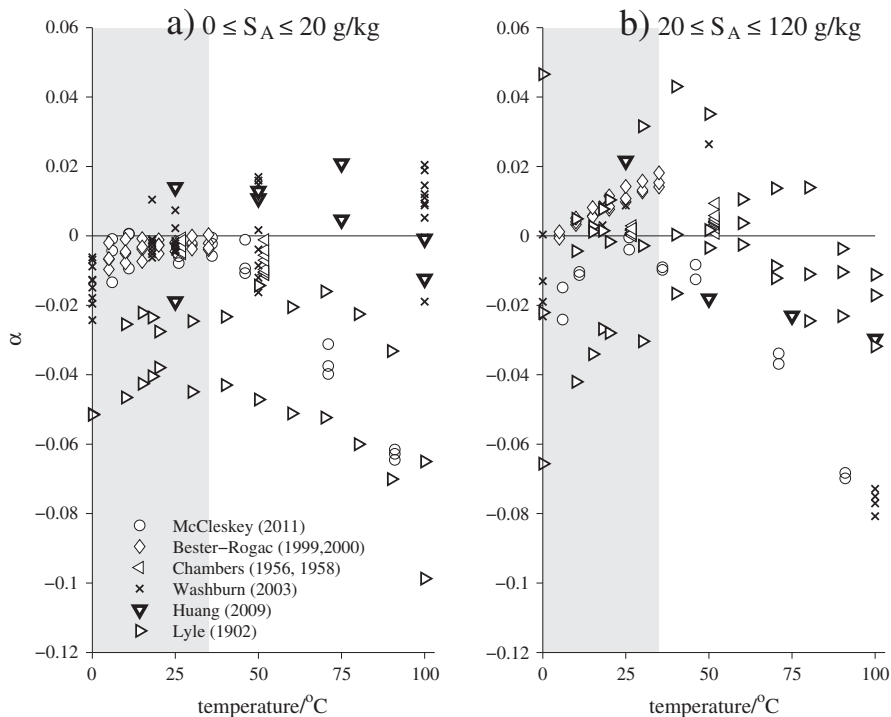

Fig. 5. Variations of α with temperature, for (a) low salinities and (b) high salinities. Shaded region represents Neptunian temperatures.

an error of better than 1%, and it can be used to estimate the Absolute Salinity of high-temperature seawater with an error of less than 2%. Both of these bounds are most likely set by uncertainty in measurements of the conductivity of NaCl, rather than by the inherent accuracy of PSS-78. However, although more precise measurements may therefore reduce the size of this error bound, any such reduction will likely be less than an order of magnitude.

5. Discussion

Numerical modeling successfully predicts seawater conductivities in the "Neptunian" region where precise seawater measurements have been made, and this suggests that the predictions are likely reasonably good for higher temperatures and salinities where no precise seawater measurements exist. The major drawback of this approach is that the NaCl measurements used as a baseline have a scatter almost two orders of magnitude larger than that of the precise seawater measurements used to create PSS-78. This is not because the NaCl measurements are flawed, at least relative to typical measurements in the chemical literature, but rather because the careful seawater measurements carried out in support of PSS-78 were of unusual precision. A second drawback is that the available data for high salinities at very high temperatures are inconsistent. These drawbacks limit the ultimate accuracy of comparisons. However, careful analysis of the different sets of measurements suggests that the PSS-78 algorithm embedded in TEOS-10 remains remarkably useful as a tool for characterizing seawater, even outside its stated region of validity, albeit at a reduced accuracy.

An important caveat is that the analysis has assumed that the relative chemical composition of the seawater remains approximately constant. Slight changes in composition are known occur due to changes in the chemical equilibria of the carbonate system, and these are incorporated into the numerical modeling. No attempt has been made to consider the effects of added nutrients and/or river salts, but the magnitude of these effects has been considered previously and they are small relative to the overall accuracies determined above. However, freezing seawater, or bringing it to high temperatures and/or evaporating it can lead to larger changes in relative composition due to the precipitation of salts. Precipitation will decrease the amount of dissolved matter, and hence can decrease the electrical conductivity, but more importantly will change the relative composition and hence conductivity/salinity/density relationships.

During freezing $CaCo_3$ may precipitate at a temperature somewhere between −1.9 and −3.5 °C when $CaCo_{3(s)}$ crystals are present, but as low as −4.9 °C in "open water" [30]. Brines in sea ice at lower temperatures will therefore have a modified composition, but the details of this composition can vary depending on the reaction path [31]. Thus no conclusions can yet be drawn about conductivity/salinity relationships of brines trapped in sea ice.

During evaporation the first salt to precipitate is usually $CaCo_3$ in the form of calcite or aragonite, followed by gypsum ($CaSO_4 \cdot 2H_2O$) [13]. Halite (NaCl) precipitates next, but only when less than 10% of the original water is left (salinities $\gg$ 200 g/kg). However, the precipitation process is not purely dependent on ambient temperature and salinity. An important factor controlling carbonate precipitation is the concentration of CO_3^{2-}, and this concentration is not directly proportional to salinity. This is because there is a chemical equilibrium between CO_3^{2-} and other components of the carbonate system, which include dissolved CO_2. This gas may or may not be equilibrated with atmospheric levels, and can also vary due to biological activity. Lowering the concentrations of CO_2 (or equivalently increasing pH) can promote precipitation [32].

Model calculations performed by Marion et al. [30] determined a precipitation limit in open-water systems without biological activity, but equilibrated to the atmosphere, at temperatures less than 40 °C. Typically carbonate precipitation occurs at salinities of about 70 to 80 g/kg, with the critical salinity decreasing at higher temperatures (Fig. 1). Extrapolating this curve to even higher temperatures suggests that precipitation will probably not occur in Neptunian seawaters as they are heated to boiling, but that even a small amount of evaporation at these high temperatures may result in precipitation.

This sensitivity at high temperatures is well known to phycologists needing to sterilize seawater as a medium for culturing phytoplankton. Autoclaving seawater at 121 °C (at $p \approx 1$ atm) will result in precipitation of carbonates with calcium, magnesium, and other trace constituents [33]. This can be avoided by first decreasing the pH [34]. However, heating to only 95 °C for long periods ("tyndallization") avoids precipitation without the need for other manipulations.

Behavior in evaporating brines in contact with sediments and/or subject to biological activity is even more complex. Rough generalizations suggest calcite begins precipitating when about two-thirds of the water has been evaporated in natural systems (presumably at temperatures of 20–40 °C), i.e. salinities of about 100 g/kg, but in artificial environments precipitation can begin when only half the water is gone, i.e. salinities of around 65 g/kg [13]. High-salinity waters can also become anoxic. Then, in addition to precipitation, anaerobic biological processes can reduce sulfate to hydrogen sulfide gas, which may be lost to the atmosphere.

However, the existence of these processes does not completely invalidate the unmodified use of PSS-78. As an upper bound, Ca^{2+} represents about 1% of the mass of dissolved matter in seawater, carbonates only about 0.4% and sulfate about 8% [1]. Thus conductivity, salinity, and density changes will only be of that order or smaller, as changes in the number of ions are partially compensated in conductivity measurements. In addition, not all of these constituents will be lost before the point of halite precipitation, so the actual induced error will be even less. For example, autoclaving unmodified seawater results in precipitation of only around 0.05% of the dissolved material [33].

Acknowledgements

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