



Ocean chemistry and the speed of sound in seawater



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ABSTRACT

For over 50 years scientists have represented the speed of sound in sea water (V) as an ad hoc high order polynomial with up to 42 coefficients linking temperature, pressure, and salinity, or via an equation of state with 104 coefficients. While this has allowed accurate calculation of sound speed profiles, these are formulations with no underlying molecular basis. We show that a simple van 't Hoff formulation with a plot of $\ln V$ versus $1/T$, where T is the absolute temperature, as a basis leads to a simpler formulation with minimal error with at most only 28 coefficients required. This finding suggests that the dominant control on the speed of sound within the oceanic range appears to have the form of simple reversible equilibria within the water structure system and that V mimics, or may be treated as resulting from, a simple pressure perturbation between apparent equilibria within the water structures. The van 't Hoff slope is indicative of an endothermic reaction in which the sound wave loses energy into the ocean. Since sound speed profiles are fundamentally separable into their temperature and depth (pressure) dependencies their partial correlation with some chemical profiles appears to offer a potentially powerful proxy for separating the typically comingled properties of temperature and depth in describing ocean chemical profiles and rates.

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1. Introduction

An ocean chemical control on sound absorption in the ocean has long been recognized (Mellen and Browning, 1977; Hester et al., 2008), but a parallel connection between sound speed and the chemistry of sea water has proved difficult to identify; here we explore this relationship.

1.1. Historical background

For over fifty years the development of equations for the speed of sound in sea water proceeded simply as a result of statistical analysis. Wilson (1960) measured “a total of 581 sound speeds at fifteen temperatures, eight pressures, and five salinities”. He then obtained 22 coefficients “by forming a 20×20 matrix... and solving using the method of least squares” thereby creating a useful but complex relationship between sound speed (V) and T , P , and S properties but with no underlying basis in physical chemistry.

These coefficients served well for over a decade when a re-determination of the sound speed was undertaken. Del Grosso and Mader (1972a) reported 148 measurements of the speed of sound in pure water reported as a function of T by least squares fit with a reproducibility of “better than 4 ppm” and reported as a fifth-degree polynomial in temperature on the T_{68} scale. This was accompanied by 627 equally careful replicate observations on the speed of sound in sea-water samples (Del Grosso and Mader, 1972b). The samples measured were derived from Standard Sea Water ampules (Batch P₄₆ 12/4/1966 19.377‰ Cl) “modified to salinities in the range 33 to 39‰”. From these a 23-term polynomial equation was derived to fit the data. Cautions that the specification of “salinity” as used in these experiments may not be suitable beyond “mid-ocean” regions were mentioned, but considered beyond the scope of the article, thus foreshadowing later chemical interests.

Del Grosso (1974) gave equations and prepared tables for the speed of sound in natural waters with a total of 19 coefficients, but with a carefully restricted range described as “The tables have been prepared with attention to realistic triads of S , T , and P , so the salinity parameter considered in Table I is 29, 35, and 41 ppt but only 33, 35, and 37 in Table II” thereby sacrificing generality for practicality in observing the narrow range of properties in much of the deep ocean. When we have explored the use of the Del Grosso (1974) coefficients beyond this narrow range we find that the calculated sound speeds are very rapidly diverge from all other formulations of sound speed in sea water suggesting that the coefficients are exceptionally narrowly tuned.

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Chen and Millero (1977) independently measured the speed of sound in sea water at high pressure, and at varying salinities and temperatures. They again used the method of least squares to produce a high order polynomial to fit the data. The Chen and Millero (1977) results form the basis for the widely used UNESCO equation for sound speed (Fofonoff and Millard, 1983). The above ensemble of equations have for decades served an essential purpose and are widely used in ocean science. This work was extended by Wong and Zhu (1995) to bring it in line with the International Temperature Scale of 1990. This produced a complex formula that has some 42 coefficients which contain cross products in salinity, temperature and pressure.

It is difficult to find a “best” solution amidst the complex formulations with a long concatenation of coefficients; Dushaw et al. (1993) did conclude from analysis of long range transmissions across a very limited range of S, T and P, that the arrival times were in better agreement with the formulation of Del Grosso (1974), and this conclusion was independently supported by Meinen and Watts (1997). But these findings are empirical and do little to address the best solution based on the underlying chemical physics. The finding that several field experiments suggested better agreement with the Del Grosso (1974) data has been carefully addressed by Millero and Li (1994) with the finding that this originated from “the unreliable sound speeds for pure water determined by Wilson (1959) at low temperatures and high pressures.” A correction was provided to account for this.

1.2. The international Thermodynamic Equation of State – TEOS-10

An independent and highly developed approach to calculating sound speed is provided via the international Thermodynamic Equation of State (TEOS-10) for sea water (IOC et al., 2010) based upon a Gibbs function intended to be thermodynamically consistent across all physical properties. In this equation care is taken to use absolute salinity, thus accounting for changes in the chemical composition of sea water with depth and with region. The speed of sound is then computed directly from the calculated isentropic and isohaline compressibility with high accuracy if the composition is known. However this calculation is challenging for even the “computationally efficient” form requires a 75-term polynomial, and the full version of the algorithm contains some 104 coefficients.

Earlier investigators did not take into account variability in sea salt chemical ratios, and since attention to basic chemical principles is at the heart of this paper this is worth reviewing in some detail here. The classical example of this is found in examining the mixing between riverine and oceanic waters in the extensive brackish region of the Baltic Sea. Wirth (1940) first provided an analysis of this problem based upon the molal volumes of the major species present. He correctly identified a small error in that the computed densities of Baltic Sea water were slightly higher than those from the standard hydrographic tables of Forch et al. (1902). Brewer and Bradshaw (1975) extended this work into the modern era by identifying anomalies, derived from partial equivalent conductances and partial molal volumes, in the major ocean basins based on the conductivity–salinity–density relationship. From this it was clear that the density of deep Pacific Ocean water was slightly underestimated by conductivity based salinity measurements and this analysis was soon confirmed by the direct measurements of Millero et al. (1976).

The matter of the influence of sea water chemistry anomalies has been investigated extensively in recent years (Millero et al., 2008; Pawlowicz, 2008; Feistel et al., 2010), and from this work it is now possible to derive the regionally varying absolute salinity for use in calculating thermodynamic properties.

1.3. Analysis

The purpose of this paper is not to provide a judgment as to which data set is “better” but to ask whether a more fundamental underlying

principle may be found that would provide improved rigor and simplicity in formulating a sound speed equation no matter which experimental data set is used.

In examining the now more than 50 year-long efforts to provide an accurate representation of the speed of sound in sea water we have gone from requiring 22 coefficients (Wilson, 1960), to 42 coefficients (Wong and Zhu, 1995), to either 75 or 104 coefficients as required by TEOS-10. This continuing increase of coefficients suggests that an alternate formulation based upon fundamentally different underlying principles may be simpler and useful. The earlier works simply provided best-fit polynomials in T, P, and S with no chemical basis. The TEOS-10 formulation is very carefully based upon a Gibbs function of sea water composition; but this makes use of the bulk thermodynamic properties of solutions, not dynamic molecular processes. It also runs into a small but nagging internal thermodynamic inconsistency: the isentropic compression of sea water is treated as a fully reversible process with no entropy gain. But the compression of sea water by a sound wave is work and, although the effect is small, entropy is inevitably gained. In practice sound speed and sound absorption are inextricably linked by the temperature and pressure dependent structure of water and salts.

2. Lessons learned from the structure of water

Over the last decade or so considerable progress has been made in investigating the structure of water, much of this derived from Raman spectroscopy. With the development of deep-sea Raman spectrometers for experimental work in situ at ocean depths (Brewer et al., 2004; Zhang et al., 2012) ocean scientists can see very clearly at sea and in real time the changing structure of water. This is dominated by the hydrogen bonded five-molecule tetrahedral structure, with T, P, and S dependencies in nature consistent with laboratory pressure cell experiments (Walrafen et al., 1986; Terpstra et al., 1990). The water ν_2 bending mode, with known weak T, P, and S dependence, is frequently used as an internal standard to quantify the spectra obtained (Dunk et al., 2005; Zhang et al., 2011).

The transient pressure pulse of a sound wave perturbs these structures in a consistent manner. Possibly the clearest explanation of this is provided in the paper by Carey and Korenowski (1998) in which the Raman band structures are investigated, and carefully deconvoluted, as functions of temperature and pressure. The water structures are shown to exist in T and P equilibrium and thus can be well described by the classic van 't Hoff equation (van 't Hoff, 1884). The Raman “librational” modes decrease in frequency with rising temperature since the force constants decrease as hydrogen bonding decreases. This may provide a simple account of the increasing speed of sound in water with increasing temperature as the structure slowly moves towards the configuration the water would have in the gas phase. The experimental determination of the effects of T and P on water structure is supported by molecular dynamics simulations (Canpolat et al., 1998).

Carey and Korenowski (1998) used the simple form of the van 't Hoff (1884) expression to calculate the hydrogen bond strength that dominates the changing water structure. For this the partial derivative of $\ln K$ with respect to the inverse absolute temperature with pressure held constant is used as in:

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H}{R}.$$

In this manner the hydrogen bond enthalpy change was calculated as 2.53 kcal/mol and found to be in excellent agreement with previously published values.

These findings, both experimental and theoretical, strongly suggest that the effect of a pressure pulse (sound wave) can reasonably be

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