

Scattering by pure seawater at high salinity

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Abstract: A new model for seawater scattering was developed, in which Gibbs function was used exclusively to derive the thermodynamic parameters that are associated with density fluctuation. Because Gibbs function was determined empirically from highly accurate measurements of a group of thermodynamic variables and is valid for S_A up to 120 g kg⁻¹ (Deep-Sea Research I, 55, 1639, 2008), we expect the model is also valid over the extended range of salinity. The model agrees with the measurements by Morel (Cahiers Oceanographiques, 20, 157, 1968) with an average difference of -0.6% for $S = 0$ and 2.7% for $S = 38.4$. The scattering by seawater as predicted increases with salinity in a non-linear fashion, and linear extrapolation of scattering based on Morel's measurements would overestimate by up to 30%. The extrapolation of ZHH09 model (Optics Express, 17, 5698, 2009), which is valid for S_A up to 40 g kg⁻¹, however, agrees with the prediction within $\pm 2.5\%$ over the entire range of salinity. Even though there are no measurements available for validation, the results suggested that the uncertainty is limited in using the newly developed model in estimating the scattering by seawater of high salinity.

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1. Introduction

Light scattering by seawater is an inherent optical property of fundamental importance in oceanic optics. Morel [1,2] measured the scattering by pure water and natural seawater of salinity $S = 38.4$ at five wavelengths of 366, 405, 436, 546, and 578 nm and found an average increase of 30% by seawater over pure water. For the past 4 decades, the measurements by Morel at one salinity value have been used throughout global oceans and coastal waters [e.g., 3], though sometimes adjusted linearly as a function of salinity [e.g., 4]. Recently, Zhang et al. [5] deduced thermodynamically the effect of sea salts on the scattering by seawater and found that scattering increases with salinity non-linearly. Their results agreed with Morel's measurements within his experimental error of 2%.

From the fluctuation theory [6], the scattering by pure seawater, here represented by the volume scattering function at 90 degree, $\beta(90)$, is due to two independent contributions:

$$\beta(90) = \beta_d(90) + \beta_c(90), \quad (1)$$

where $\beta_d(90)$ and $\beta_c(90)$ are the scattering due to density and concentration (mixing ratio) fluctuations, respectively. Following Zhang and Hu [7] and Zhang et al. [5], the terms $\beta_d(90)$ and $\beta_c(90)$ can be further expressed as,

$$\beta_d(90) = \frac{\pi^2}{2\lambda^4} \left(\rho \frac{\partial n^2}{\partial \rho} \right)_T^2 k T \beta_T f(\delta) \quad (2)$$

and

$$\beta_c(90) = \frac{\pi^2}{2\lambda^4 N_A} \left(\frac{\partial n^2}{\partial S} \right)^2 \frac{M_w}{\rho} \frac{S}{-\partial \ln a_w / \partial S} f(\delta). \quad (3)$$

respectively, where λ is the wavelength, k the Boltzmann constant, N_A the Avogadro number, ρ , n , T , β_T , S and $f(\delta)$ are the density, the refractive index in vacuum, the absolute temperature, the isothermal compressibility, the salinity and the Cabannes factor of seawater, respectively, and a_w and M_w are the activity and molecular weight of water in seawater, respectively.

Some natural water bodies exhibit extremely high salinity. Tropical estuaries like the Australian Shark Bay show salinities up to 70 g kg⁻¹ [8], and desiccating seas like the Dead Sea even approaches saturation concentration. While in theory both Eqs. (2) and (3) can be applied to these high salinity waters, their practical use is limited by the validity ranges of the parameters (ρ , n , β_T , and a_w) that have been empirically determined for T up to 30 °C and S up to 40. With no measurements available on scattering by seawater at high salinity, the uncertainty associated with extrapolation is unknown. Another minor issue is that Practical Salinity Scale S used in Eq. (3) is undefined for $S > 42$ [9].

Recently, Feistel [10] developed a new general equation of state for seawater in the form of the specific Gibbs energy of seawater from experimental data of heat capacities, freezing points, vapor pressure and mixing heat. The developed Gibbs function, $g(S_A, T_c, p)$, where S_A is the absolute salinity in g kg⁻¹, T_c the temperature in Celsius, and p sea pressure in Pa, has an extended range of validity for $0 \leq S_A \leq 120$ g kg⁻¹, -12 °C $\leq T_c \leq 80$ °C, and -0.1 Pa $\leq p \leq 100$ MPa. Since the thermodynamic parameters, ρ , β_T , and a_w as used in Eqs. (2) and (3) can all be derived mathematically from Gibbs energy through partial derivatives of g with respect to S_A ,

T_c , p , or their combinations, we expect that their values thus derived are also valid over the extended ranges. The purposes of this study are to develop a light scattering model for seawater that is based on Gibbs function and to estimate the scattering for high salinity waters.

2. A scattering model based on the Gibbs function

The mass specific Gibbs energy of a seawater sample containing the mass of water m_w , and the mass of salt m_s , at temperature T_c , and sea (gauge) pressure p ,

$$g(S_A, T_c, p) = \mu^W + S_A(\mu^S - \mu^W) \quad (4)$$

where μ^W and μ^S are the chemical potential of water in seawater and of salt in seawater, respectively, and $S_A = m_s/(m_w + m_s)$ is the absolute salinity [9]. Using extremely accurate measurements for density, heat capacity, vapor pressure, boiling temperature, freezing temperature, relative enthalpy and sound speed, and theoretical relations like the Debye-Hückel limiting law, multivariate polynomial functions of orders up to 7 were determined for μ^W [11] and μ^S [10], respectively. Denoting the respective polynomial function as $g^W(T_c, p)$ and $g^S(S_A, T_c, p)$, Eq. (4) becomes

$$g(S_A, T_c, p) = g^W(T_c, p) + g^S(S_A, T_c, p) \quad (5)$$

with the property $g^S(0, T_c, p) = 0$. Also it is apparent from Eq. (5) that $\partial g / \partial S_A = \partial g^S / \partial S_A$.

The osmotic pressure ϕ of seawater can be defined by the difference between the Gibbs potential of pure water and of water in seawater. Following Eq. (5).19) of Feistel and Marion [12] and Eq. (7).7) of Feistel [10],

$$-mRT\phi = g^S(S_A, T_c, p) - S_A \frac{\partial}{\partial S_A} g(S_A, T_c, p) \quad (6)$$

where m is the molality (moles of salt per mass of water) and $R = N_A \times k$ the molar gas constant. The water activity, a_w , is linked with the osmotic pressure [13],

$$\ln a_w = -mM_w\phi \quad (7)$$

Combination of Eqs. (6) and (7) gives,

$$\frac{\partial \ln a_w}{\partial S_A} = \frac{M_w}{RT} \frac{\partial}{\partial S_A} (g^S - S_A \frac{\partial g^S}{\partial S_A}) = -\frac{M_w}{RT} S_A \frac{\partial^2 g^S}{\partial S_A^2} = -\frac{M_w S_A}{RT} g_{ss}. \quad (8)$$

Hereafter, we will use subscripts of s , t , or p after the letter g to denote the partial derivative of the Gibbs function with respect to the variables of S_A , T_c , or p . Thermodynamically, the isothermal compressibility can be derived from the Gibbs energy as

$$\beta_T = -\frac{g_{pp}}{g_p}, \quad (9)$$

and density as

$$\rho = \frac{1}{g_p}. \quad (10)$$

Inserting Eqs. (8) and (10) into Eq. (3) and using Eq. (9), we have,

$$\beta_c(90) = \frac{\pi^2}{2\lambda^4} \left(\rho \frac{\partial n^2}{\partial \rho} \right)^2 \beta_T kT \left(-\frac{g_{ps}^2}{g_{pp}g_{ss}} \right) f(\delta). \quad (11)$$

Equation (11) is the same as Eq. (2) except for a multiplication factor $(-g_{ps}^2/g_{pp}g_{ss})$, which is attributable to the variations of density (Eq. (10)) with salinity (g_{ps}) and pressure (g_{pp}) and the variation of chemical potential (g_s) with salinity (g_{ss}). The similarity between Eq. (2) and Eq. (11) simply reiterates the fact that the underlying physics for scattering by a pure liquid and by a mixture is the same: density fluctuation. With Eqs. (11) and (9), the total scattering by seawater, Eq. (1), can be rewritten as:

$$\beta(90) = \frac{\pi^2 kT}{2\lambda^4} \left(\rho \frac{\partial n^2}{\partial \rho} \right)^2 \left(-\frac{g_{pp}}{g_p} + \frac{g_{ps}^2}{g_p g_{ss}} \right) f(\delta). \quad (12)$$

The term $\rho(\partial n^2/\partial \rho)$ in Eq. (12) has been derived theoretically and empirically as a function of n [7]. The refractive index of seawater has been determined experimentally over the typical ranges of S (0 – 40) and T_c (0 – 30°C) under normal pressure [e.g., 14]. For a given temperature and pressure, the values of n were found varying with salinity linearly [14,15]. Because of this, the empirical relationship developed by Quan and Fry [16] based on the data set [14] for $S < 40$ will be extrapolated to estimate n over the extended salinity range. The details on how to estimate the terms $\rho(\partial n^2/\partial \rho)$ and n can be found in Table 1 of Ref [5].

One advantage of Eq. (12) is that all the thermodynamic variables that are needed to estimate scattering are derived from a single parameter, Gibbs energy. While this does not necessarily translate into a better estimate, because g is also empirically determined, it does ensure that the inter-relationships among different thermodynamic variables are always satisfied. The independent variables for Eq. (12) are temperature T_c (or T , $T = 273.15 + T_c$), sea pressure p (or absolute pressure P , $P = 101325 \text{ Pa} + p$), and absolute salinity S_A (within the definition range of Practical Salinity Scale, S , $S_A (\text{g kg}^{-1}) = 1.0047 S$ [9]).

From Eq. (12), the volume scattering function, $\beta(\theta)$, at the scattering angle, θ , or the total scattering coefficient, b , can be calculated as:

$$\beta(\theta) = \beta(90) \left(1 + \frac{1-\delta}{1+\delta} \cos^2(\theta) \right) \quad (13)$$

$$b = \frac{8\pi}{3} \beta(90) \frac{2+\delta}{1+\delta}. \quad (14)$$

3. Results and discussion

Theoretically, Eq. (12) is the same as our previous model [5, referred to as ZHH09 hereafter]. The spectral scattering by seawater estimated by Eq. (12) were compared with predictions by ZHH09 for $S = 0$ and $S = 38.4$, at which the laboratory measurements were carried out by Morel [1,2]. The results are shown in Fig. 1. A value of 0.039 for the depolarization ratio parameter, δ [17] was used for Fig. 1 and the rest of calculations.

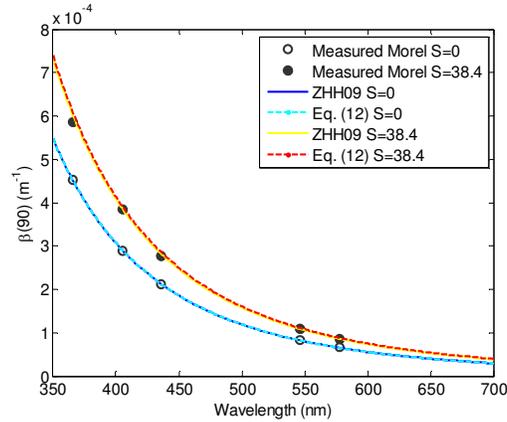


Fig. 1. Spectral scattering of seawater estimated using Eq. (12) and ZHH09 for $S = 0$ and 38.4 and $T_c = 20^\circ\text{C}$ are compared with Morel's measurements.

For pure water ($S = 0$), both models perform the same, with an average difference with the measurements of -0.6% . For seawater ($S = 38.4$), Eq. (12) slightly underperforms ZHH09 with an average difference with the measurements of 2.7% vs. 1% . Gibbs function used in Eq. (12) was empirically fitted against a group of thermodynamic data sets covering an extended range of temperature ($-6 - 80^\circ\text{C}$) and salinity (up to 120 g kg^{-1}) [10], while the thermodynamic parameters used in ZHH09 are fitted against the measurements of individual parameters directly. For example, the activity of water a_w in Eq. (3) was derived by directly fitting the measured values [13] for $S < 40$ to a general Debye-Hückel form as a function of temperature and salinity [5]. On the other hand, data sets used in deriving Gibbs function and hence a_w were diverse in order to cover a wider range of temperature and salinity, though they are related thermodynamically. Considering this as well as the fact that the relative experimental error was $\sim 2\%$, we feel comfortable in applying Eq. (12) for seawater with extreme salinities.

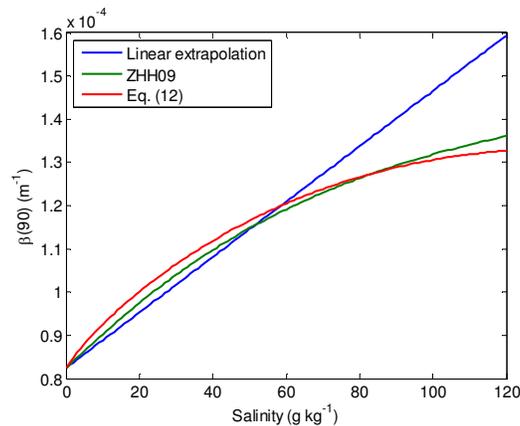


Fig. 2. Scattering of seawater are estimated for $\lambda = 546 \text{ nm}$ and $T_c = 20^\circ\text{C}$ as a function of absolute salinity using Eq. (12), ZHH09 model, and linear extrapolation (Eq. (3) of Ref. 5).

The scattering of seawater as a function of salinity from 0 to 120 g kg^{-1} calculated using Eq. (12) at 546 nm and 20°C is shown in Fig. 2. For comparison, the estimates by ZHH09 model and by extrapolation of linear assumption [4, Eq. (3) in 5] are also shown. Overall, the scattering increases with salinity. But clearly the variation is non-linear, which is due to a combination of two factors: decreasing contribution due to density fluctuation and increasing

contribution due to concentration fluctuation, with latter effect dominating [5]. The linear assumption underestimates the scattering at low salinities but the extrapolation will overestimate the scattering at high salinities, with an error up to 30% at $S_A = 120 \text{ g kg}^{-1}$. Twardowski (personal communication) observed a similar pattern of variation in scattering by NaCl solutions with concentrations up to 100 g kg^{-1} . It is interesting to note that Eq. (12) and ZHH09 model agree to each other within $\pm 2.5\%$ over the entire range of possible salinity values. Considering that the parameters used in the two models were derived quite differently, their close agreement with each other suggests that both models are theoretically sound and also confirms that the measurements that were used to derive the thermodynamic parameters were of high quality [10,18].

The uncertainty of using Eq. (12) or ZHH09 model at high salinity is unknown because no measurement is available for comparison. Given their good agreement with Morel's measurements and their consistent agreement with each other over the entire range of salinity, we expect that the uncertainty of using either of them at high salinity is limited. However, because ZHH09 model agree with Morel's measurements within the experimental error of 2% (1% for ZHH09 and 2.7% for Eq. (12)) and because the Gibbs function used in Eq. (12) was fitted for S_A up to 120 g kg^{-1} , we recommend that 1) for S (or S_A) < 40 (or 40 g kg^{-1}), use ZHH09 model; and for higher salinity, use Eq. (12).

Since the Gibbs function is expressed in terms of absolute salinity, it applies to seawater with small composition anomalies [10]. In such cases, density (Eq. (10)), as the most sensitive property in this respect, is independent of small chemical composition variations if expressed in terms of absolute salinity [9]. We assumed that uncertainties of other two thermodynamic parameters, β_T (Eq. (9)) and a_w (Eq. (8)), and hence Eq. (12) associated with small chemical composition variations are also negligible. While we focused in this study on high salinity, Eq. (12) applies to seawater with high temperature or under high pressure as well. The variations of scattering with temperature or pressure, however, are much smaller as compared to the variations due to salinity. For example, the scattering decreases $\sim 1.4\%$ from surface to a depth of 1000 meters; and the scattering remains about the same (within 0.5%) between 26°C and 60°C . The spectral signature varies marginally with salinity (solely due to n), with the power-law slope varying from -4.29 to -4.32 for S_A from 0 to 120 g kg^{-1} .

In our previous studies, we discussed the uncertainties associated with the depolarization ratio, δ : its absolute value for pure water [7] and its variation with sea salts [5]. Assuming the possible value of δ is between 0.03 and 0.05, roughly $\pm 25\%$ variation about 0.039, a value adopted in this study, $\beta(90)$ or b would vary approximately $\pm 2\%$. However, the exact behavior of δ for seawater is still unknown. To further constrain the uncertainty in scattering by seawater, a fundamental quantity in ocean optics, the next challenge would be to improve our understanding of δ and its variation with salinity.

4. Conclusions

We developed a new model for seawater scattering, in which Gibbs function was used exclusively to derive the thermodynamic parameters that are associated with density fluctuation. The Gibbs function, determined from highly accurate experimental data of heat capacities, freezing points, vapor pressures and mixing heats, is valid in the range -6 to 80°C in temperature and 0 - 120 g kg^{-1} in absolute salinity. And we expect the model (Eq. (12)) based on Gibbs function would also be valid for the extended ranges. The purpose is to provide a first-order estimate of seawater scattering at high salinity because no measurements are available. The agreement of Eq. (12) with Morel's measurements, -0.6% for $S = 0$ and 2.7% for $S = 38.4$ and consistent agreement with ZHH09 model for $S_A = 0 - 120 \text{ g kg}^{-1}$, seemed to suggest the uncertainty in using Eq. (12) for high salinity waters is limited. The Matlab code implementing Eq. (12) can be downloaded at <http://www.und.edu/instruct/zhang>.

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