

# Scattering by pure seawater: Effect of salinity

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**Abstract:** A theoretical model was developed estimating the scattering by seawater that are due to concentration fluctuation. Combining with the model proposed for density fluctuation (Optics Express, 17, 1671, 2009), we evaluated the overall effect of sea salts on the scattering. The variation of seawater scattering with the salinity is a combination of two factors: decreasing contribution due to density fluctuation and increasing contribution due to concentration fluctuation, with the latter effect dominating. The trend is, however, slightly non-linear and the linear adjustment of scattering with salinity that is frequently used would lead to an underestimate by an average of 2%. The results estimated at  $S = 38.4\text{‰}$  agree with the measurements by Morel (Cahiers Oceanographiques, 20, 157, 1968) with an average difference of 1%, well within his experimental error of 2%. The spectral signature also varies with salinity, with the power-law slope increasing from -4.286 to -4.306 for salinity from 0 to 40‰.

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**OCIS codes:** (010.0010) Atmospheric and oceanic optics; (010.4450) Oceanic optics; (290.5840) Scattering, molecules.

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## 1. Introduction

Scattering by pure water or pure seawater is a quantity of fundamental importance in aquatic optics. The contribution by these hypothetically pure liquid, often used as a "blank", must be subtracted from the observed scattering in order to derive the properties of particles that are often of primary interest. According to Einstein-Smoluchowski theory [1], the scattering of light by a particle-free liquid is due to the microscopic fluctuation of its dielectric constant ( $\epsilon$ , or equivalently, the refractive index,  $n$ , where  $\epsilon = n^2$ ), which in turn is caused by localized fluctuations in density and mixing ratio (i.e., concentration). Representing the scattering with the volume scattering function at 90 degree,  $\beta(90)$ , then

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

where  $\beta_d(90)$  and  $\beta_c(90)$  are the scattering due to density and concentration fluctuation, respectively.

Recently we [2] evaluated theoretically the scattering by pure water, which is due to density fluctuation entirely.

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

where  $\lambda$  is the wavelength,  $k$  the Boltzmann constant, and  $\rho$ ,  $n$ ,  $T$ ,  $\beta_T$  and  $f(\delta)$  are the density, the refractive index in vacuum, the absolute temperature, the isothermal compressibility, and the Cabbanes factor of water, respectively. Table 1 lists the details of these parameters including their estimates and the associated errors. Theoretical calculation using the model that we proposed for estimating the density derivative of the refractive index ( $\rho(\partial n^2/\partial \rho)$ ) [3] agrees with Morel's measurements within the experiment error (2%) with an average difference ranging from -0.67% to 1.97% for values of  $\delta$  varying from 0.039 to 0.051 [4].

Presence of sea salts induces additional fluctuations in the concentration leading to additional scattering. Morel [5, 6] measured the scattering by natural seawater of salinity  $S = 38.4\text{‰}$  at five wavelengths of 366, 405, 436, 546, and 578 nm and found an average increase of 30% over the pure water. To our best knowledge, there have been no other measurements reported evaluating the effect of sea salts on the scattering of seawater. While its contribution to the total scattering is generally small, up to 10% in the visible for very clear ocean waters, seawater can account for a sizable portion of total backscattering, up to 80% in the clearest waters [7-9], owing to its nearly isotropic characteristics of angular distribution. In alpine lakes, the contributions to the backscattering by water are also significant (30-60%) [10].

For the past 4 decades, the values observed by Morel at one salinity value have been used throughout global oceans and coastal waters [e.g., 11], though sometimes modified via a linear adjustment as a function of salinity [e.g., 12]. Based on the interpretation in Morel [13], Boss and Pegau [12] proposed an empirical model for adjusting the seawater scattering,

$$\beta(90) = \beta_{pw}(90) \left(1 + \frac{0.3}{S_0} S\right) \quad (3)$$

where  $\beta_{pw}(90)$  is the scattering of pure water and  $S_0=37$ . Given that the reported salinity for the natural seawater that Morel measured was 38.4‰, a value of 38.4 for  $S_0$  may be more exact.

The linearity assumption is only valid when salinity approaching zero, namely, the solution is ideal, under the condition of which Morel [13] used a simple model to estimate the excessive scattering following Debye [14],

$$\beta_c(90) = \frac{\pi^2 M_{ss} S}{2\lambda^4 N_A} \left(\frac{\partial n^2}{\partial S}\right)^2 \frac{f(\delta)}{\rho} \quad (4)$$

where  $N_A$  is the Avogadro number,  $M_{ss}$  represents the mean molecular weight of the electrolyte, and  $S$  the mass concentration of solute with a unit of g/kg. For seawater,  $S$  in Eq. (4) differs from the Practical Salinity  $S$  (‰) in both definition and values,  $S(\text{g/kg})=1.0047 \times S(\text{‰})$  [15]. But we will use them interchangeably, because the results will be barely affected. Equation (4) was also used by Jonasz and Fournier [16] and its variation with  $S$  having a unit of g/l by Shifrin [17] to estimate scattering due to sea salts. Note, the term  $1/\rho$  in Eq. (4) was not present in Morel [13] or Jonasz and Fournier [16]; it is required either from theoretical deduction or from dimensional analysis. However, because  $\rho$  would take a unit of kg/l and hence have a value close to unity, their computations are still valid numerically. The term  $\partial n^2/\partial S$  in Eq. (4) can be assumed as a constant (within 0.6%) for a given temperature and wavelength [18], which leads to a prediction of linear variation of  $\beta_c(90)$  with  $S$ . Apparently, if the effect of  $\rho$  is considered, the linearity between  $\beta_c(90)$  and  $S$  will no longer be warranted.

The development of Eq. (4) was based on the assumption that the solution of two components is dilute and ideal. Even though seawater can be deemed as a dilute solution and the composition and proportion of its sea salts remains constant fairly well over global ocean, it is well known that an electrolyte solution such as seawater is not ideal. Morel [5] measured scattering by pure NaCl solution at 366 nm and 546 nm for concentrations from 0.01 to 0.1

g/ml, and his results at 546 nm in terms of percentage increase relative to the scattering by pure water are shown in Fig. 1. Obviously, the excessive scattering due to addition of NaCl varies with the concentration in a non-linear manner. The similar pattern of non-linear variations were also found in other simple electrolyte solutions of KCl, KNO<sub>3</sub>, or NaI [19].

Seawater is a much more complex system than a NaCl solution, even though NaCl is its major sea salt. While we know theoretically that sea salts enhance the scattering, which was also confirmed by Morel's measurement, we still do not know how exactly the scattering varies with salinity, which constitutes the purpose of this study.

Table 1. Parameters used in estimating seawater scattering and their formulae for calculation

Parameters <sup>a</sup>	Ref	Formulae <sup>b</sup>
$\partial \ln a_0 / \partial S$ (0.04%)	[20]	$(a_0 + a_1 T_c + a_2 T_c^2 + a_3 T_c^3) + 1.5(a_4 + a_5 T_c + a_6 T_c^2 + a_7 T_c^3) S^{0.5} + 2(a_8 + a_9 T_c + a_{10} T_c^2) S$ $a_0 = -5.58651 \times 10^{-4}, a_1 = 2.40452 \times 10^{-7}, a_2 = -3.12165 \times 10^{-9}, a_3 = 2.40808 \times 10^{-11}$ $a_4 = 1.79613 \times 10^{-5}, a_5 = -9.9422 \times 10^{-8}, a_6 = 2.08919 \times 10^{-9}, a_7 = -1.39872 \times 10^{-11}$ $a_8 = -2.31065 \times 10^{-6}, a_9 = -1.37674 \times 10^{-9}, a_{10} = -1.93316 \times 10^{-11}$
$\frac{\rho}{\text{kg/m}^3}$ (0.0004%)	[21]	$(b_0 + b_1 T_c + b_2 T_c^2 + b_3 T_c^3 + b_4 T_c^4 + b_5 T_c^5) + (c_0 + c_1 T_c + c_2 T_c^2 + c_3 T_c^3 + c_4 T_c^4) S$ $+ (c_5 + c_6 T_c + c_7 T_c^2) S^{1.5} + c_8 S^2$ $b_0 = 999.842594, b_1 = 6.793952 \times 10^{-2}, b_2 = -9.09529 \times 10^{-3}, b_3 = 1.001685 \times 10^{-4}$ $b_4 = -1.120083 \times 10^{-6}, b_5 = 6.536332 \times 10^{-9}, c_0 = 8.24493 \times 10^{-1}, c_1 = -4.0899 \times 10^{-3}$ $c_2 = 7.6438 \times 10^{-5}, c_3 = -8.2467 \times 10^{-7}, c_4 = 5.3875 \times 10^{-9}, c_5 = -5.72466 \times 10^{-3}$ $c_6 = 1.0227 \times 10^{-4}, c_7 = -1.6546 \times 10^{-6}, c_8 = 4.8314 \times 10^{-4}$
$n^c$ (0.001%)	[18]	$d_0 + (d_1 + d_2 T_c + d_3 T_c^2) S + d_4 T_c^2 + (d_5 + d_6 S + d_7 T_c) \lambda^{-1} + d_8 \lambda^{-2} + d_9 \lambda^{-3}$ $d_0 = 1.31405, d_1 = 1.779 \times 10^{-4}, d_2 = -1.05 \times 10^{-6}, d_3 = 1.6 \times 10^{-8}, d_4 = -2.02 \times 10^{-6}$ $d_5 = 15.868, d_6 = 0.01155, d_7 = -0.00423, d_8 = -4382, d_9 = 1.1455 \times 10^6$
$n_a$ ( $1 \times 10^{-6}$ %)	[22]	$n_a = 1 + \left( \frac{k_0}{k_1 - \lambda^{-2}} + \frac{k_2}{k_3 - \lambda^{-2}} \right) \times 10^{-8}$ $k_0 = 5.792105, k_1 = 2.380185 \times 10^{-4}, k_2 = 0.167917, k_3 = 5.7362 \times 10^{-5}$
$\rho \left( \frac{\partial n^2}{\partial \rho} \right)_T$ (0.005%)	[3]	$(n^2 - 1) \left[ 1 + \frac{2}{3} (n^2 + 2) \left( \frac{n^2 - 1}{3n} \right)^2 \right]$
$\frac{\beta_T}{\text{bar}^{-1}}$ (0.01%)	[23]	$1 / [ (b_0 + b_1 T_c + b_2 T_c^2 + b_3 T_c^3 + b_4 T_c^4) + (c_0 + c_1 T_c + c_2 T_c^2 + c_3 T_c^3) S + (c_4 + c_5 T_c + c_6 T_c^2) S^{1.5} ]$ $b_0 = 19652.21, b_1 = 148.4206, b_2 = -2.327105, b_3 = 1.360477 \times 10^{-2}$ $b_4 = -5.155288 \times 10^{-5}, c_0 = 54.6746, c_1 = -0.603459, c_2 = 1.09987 \times 10^{-2}$ $c_3 = -6.167 \times 10^{-5}, c_4 = 7.944 \times 10^{-2}, c_5 = 1.6483 \times 10^{-2}, c_6 = 5.3009 \times 10^{-4}$
$f(\delta)$	[4]	$\frac{6 + 6\delta}{6 - 7\delta}, \delta = 0.039$

<sup>a</sup>The numbers in parentheses are the relative errors of estimates in percentage

<sup>b</sup> $T_c$  (0 ~ 30) is the temperature in Degree Celsius,  $S$  (0 ~ 40) is the salinity in ‰,  $\lambda$  (220 – 1100 nm) is the wavelength in nm

<sup>c</sup>The index,  $n$ , here is defined with respect to the air and therefore it has to be scaled by the refractive index of the air,  $n_a$ , to obtain the index in vacuum.

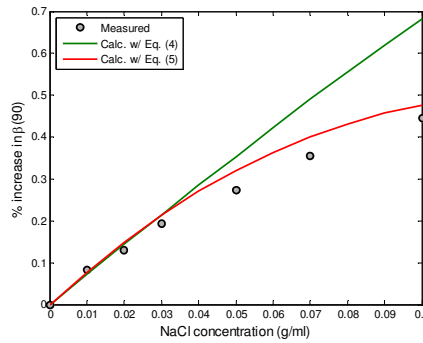


Fig. 1. Scattering by NaCl solution measured by Morel [5] at 546 nm was scaled, following the power-law of a slope of -4.30, to the sodium D line wavelength, 589 nm, at which the thermodynamic parameters for NaCl solution are available. The measured values, shown as % increases relative to the pure water, are compared with theoretical calculations using Eq. (4) and Eq. (5). The theoretical values for pure water were calculated using Eq. (2).

## 2. Scattering due to sea salts

Seawater is a multi-component solution with dissolved components of sea salts either in their original form or as dissociated ions. Complex models developed for a multi-components system by Brinkman and Hermans [24], Kirkwood and Goldberg [25], Stockmayer [26] involved the coupling terms among any two solutes, which are difficult, if not impossible, to evaluate or measure. To explain the experimental measurements of light scattering by three simple electrolyte solutions of KCl, KNO<sub>3</sub>, and NaI, Pethica and Smart [19] used an equation by Oster [27],

$$\beta_c(90) = \frac{\pi^2}{2\lambda^4 N_A} \left( \frac{\partial n^2}{\partial c} \right)^2 \frac{c \bar{V}_0}{-\partial \ln a_0 / \partial c} f(\delta) \quad (5)$$

where  $c$  is salt concentration in kg/m<sup>3</sup>,  $\bar{V}_0$  and  $a_0$  are the partial molar volume and the activity of the solvent, respectively. While still based on a two-component solution, Eq. (5) applies to the non-ideal solution with the correction term  $\partial \ln a_0 / \partial c$ . Strictly speaking, an electrolyte solution is a system of at least three components with dissociated ions and solvent. Therefore, the overall close agreement within 6% between the prediction of Eq. (5) and the measurements [19] over a wide range of concentrations suggests that Eq. (5) might be applicable to a multi-component solution like seawater as well.

In the appendix we showed that Eq. (5) would apply to seawater as long as the molar ratios among dissolved components of sea salts remain constant during the fluctuation of concentration or equivalently sea salts act like one hypothetical compound thermodynamically. This assumption was based on the following considerations. The Principle of Constant Proportion suggests that sea salts through global oceans can be regarded as one “sea salt” with major difference in their total content. In seawater, ions are paired through covalent bond, electrostatic bond, or solvent-shared electrostatic bond (separated by one or more water molecules) [28]; electrostatic interaction among ions impose some degree of order over random thermal motions [29]. Actually, it is precisely the electrostatic interactions among ions that make seawater non-ideal [29]. Also, Millero and Leung [20] have shown that many thermodynamic properties of seawater can be estimated theoretically by treating the solution as being a mixture of one hypothetical sea salt and water, and their results were in excellent agreement with the measurements. Moreover, the terms of  $\bar{V}_0$  and  $\ln a_0$  in Eq. (5) are all properties of the solvent; therefore at least part of the errors or uncertainties

associated with this assumption regarding the thermodynamic behavior of sea salts may have already been accounted for in the estimates of the thermodynamic properties of their counterpart - water.

By definitions, the partial molar volume coefficient for water,  $\bar{V}_0$

$$\bar{V}_0 = \left( \frac{\partial V}{\partial m_0} \right)_{m_{ss}} = \frac{\partial}{\partial m_0} \left( \frac{M_0 m_0 + M_{ss} m_{ss}}{\rho} \right)_{m_{ss}}, \quad (6)$$

and salinity  $S$

$$S = \frac{M_{ss} m_{ss}}{M_0 m_0 + M_{ss} m_{ss}} \quad (7)$$

Here we use the same definitions of variables as in Appendix. Deriving  $(\partial V / \partial S)_{m_{ss}}$  from Eq. (6) and  $(\partial m_0 / \partial S)_{m_{ss}}$  from Eq. (7) and taking ratio of them, we obtain,

$$\bar{V}_0 = \frac{M_0}{\rho} \left( 1 + \frac{S}{\rho} \frac{\partial \rho}{\partial S} \right), \quad (8)$$

where  $M_0$  is the molecular weight of water. The prediction of Eq. (8) agrees with the measurements of  $\bar{V}_0$  [20] within 0.05%.

Replacing the partial derivative with respect to the sea salts concentration,  $c$ , with the partial derivative with respect to the salinity,  $S$ , using the relationship,  $c = S \rho$ , and inserting Eq. (8) to Eq. (5) lead to

$$\beta_c(90) = \frac{\pi^2}{2\lambda^4 N_A} \left( \frac{\partial n^2}{\partial S} \right)^2 \frac{M_0}{\rho} \frac{S}{-\partial \ln a_0 / \partial S} f(\delta). \quad (9)$$

Equation (9) summarizes the effect of sea salts on the scattering that are due to concentration fluctuation. Equations (5) and (9) are the same; the advantage of Eq. (9) is that the refractive index, the density, and the activity for seawater have all been measured with high precision as a function of salinity.

The activity for seawater was recently estimated using a Monte Carlo simulation [30], the results agree with the experimental values [20] within 0.01%. Millero and Leung [20] fitted the measured values to a general Debye-Hückel form as a function of temperature and salinity. Combining Eqs. (14), (22), (23), (88), and (107) in Millero and Leung [20], we derived a formula for  $\partial \ln a_0 / \partial S$ , and the result is shown in Table 1, which also listed the formulae for the other parameters in Eqs (2) and (9).

If we assume that seawater is ideal, then the activity of seawater  $a_0 = (1 - X_{ss})$ , where  $X_{ss}$  is the molar fraction of sea salts and  $X_{ss} = m_{ss} / (m_0 + m_{ss})$ . Combining this and Eq. (7) leads to

$$-\frac{\partial \ln a_0}{\partial S} = \frac{M_0}{M_{ss}} \frac{1 - X_{ss}}{(1 - S)^2} \approx \frac{M_0}{M_{ss}} \quad (10)$$

Inserting Eq. (10) into Eq. (9), we will have Eq. (4). By definition,  $M_{ss}$  is the mean molecular weight of ions (dissociated sea salts) and non-dissociated sea salts dissolved in the solution. For seawater, we estimated  $M_{ss} = 31.33$  using the latest molar ratio data [15]. For aqueous NaCl solution, Morel [13] used  $M_{NaCl} / \eta$  to approximate its value, where  $M_{NaCl}$  is the molecular weight of NaCl and  $\eta=2$ , which is number of ions into which NaCl dissociates in

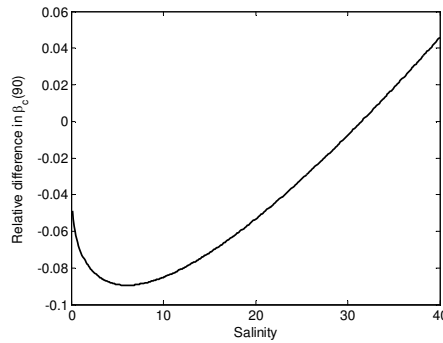


Fig. 2. The difference in  $\beta_c(90)$  of seawater estimated using Eq. (4) relative to the estimates using Eq. (9) as a function of salinity.

water. However, the theoretical mean ion weight for NaCl-type electrolyte should be  $(M_1^2 + M_2^2)/(M_1 + M_2)$  [31], where  $M_1$  and  $M_2$  represent the molecular weight of cation and anion, respectively. And mathematically,  $(M_1 + M_2)/2 \leq (M_1^2 + M_2^2)/(M_1 + M_2)$ , with equality occurs for  $M_1=M_2$ , which seldom holds for natural salt. Similarly, Johnaz and Fournier [16] used  $\sum f_i M_i / \eta_i$  to estimate the mean molecular weight of ions, where  $f_i$  is the molar fraction of sea salts and  $i$  denotes different sea salt. They derived a value of 32.41, which is bigger than the value of 31.33 that we derived based on the molar fraction of ions directly. Mathematically, these two numbers will never be equal unless all the sea salts were of the same type, e.g., 1-1 like NaCl. Given these uncertainties associated with estimating the mean molecular weight for ions as well as Eq. (4) being only an approximation, we recommend the use of Eq. (9) for estimating seawater scattering that are due to concentration fluctuation.

The differences in estimating  $\beta_c(90)$  for seawater with Eq. (4) and Eq. (9) are shown in Fig. 2. Overall, Eq. (4), which is only valid for an ideal solution, underestimates the scattering due to concentration fluctuation for salinity from 0 to 31‰ with the largest difference of -8.94% occurring at  $S=6.1‰$  and overestimates at higher salinity values. The applicable range of Eq. (9), which was derived theoretically, is determined by the validity ranges of its parameters, most of which (shown in Table 1) were determined empirically as a function of temperature, salinity, and/or wavelength. The validity range for salinity is 0~40‰. The trend shown in Fig. 2 suggests that Eq. (4) would increasingly overestimate Eq. (9) for waters with extremely high salt content. This can also be expected from a theoretical ground because the higher the concentration of electrolytes, the larger the deviation a solution would be from ideal.

The presence of sea salts also affect the scattering that is due to density fluctuation,  $\beta_d(90)$ , because all the variables of  $n$ ,  $\rho$ , and  $\beta_T$  in Eq. (2) are functions of salinity (see Table 1). Since the fluctuations due to density and concentration are independent to each other [19, 32], the total scattering of seawater is simply the sum of the two terms,  $\beta_d(90)$  and  $\beta_c(90)$ , as in Eq. (1). We should stress here that the concentration fluctuation used throughout this study refers to the change in the mixing ratio [1], because otherwise, the variations in density and concentration will not be independent.

### 3. Results and discussion

For all the calculations, we use Eq. (2) to estimate the scattering due to density fluctuation with the term  $\rho(\partial n^2/\partial \rho)$  calculated using PMH model [2] listed in Table 1. The scattering due to concentration fluctuation will be calculated using either Eq. (4), (5), or (9). The total molecular scattering for a solution is calculated using Eq. (1). Apparently, for  $S = 0$ , the

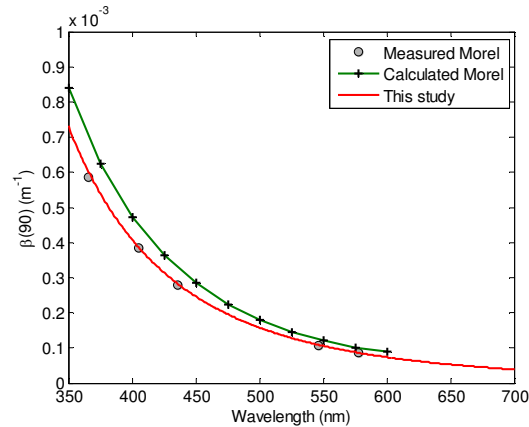


Fig. 3. Spectral scattering of seawater estimated for  $S = 38.4\text{‰}$  and  $T_c = 20^\circ\text{C}$  are compared with the measurements [5, 6] and the calculations [13] by Morel.

estimates will be the scattering by pure water. Also we use a value of 0.039 for the depolarization ratio parameter,  $\delta$  [4].

Since NaCl is the dominant sea salt among the constituents of seawater, it is of interest to evaluate how the model performs as compared to the measurements by Morel [5]. The values for the isothermal compressibility, the refractive index and the density of NaCl solution are from Handbook of Physics and Chemistry [33] and the values for the activity are from Pitzer and Mayorga [34]. The prediction based on the assumption that an electrolyte solution is ideal (Eq. (4), and green curve in Fig. 1) would overestimate significantly at higher concentrations. On the other hand, the estimate by Eq. (5) (red curve) can largely account for the observed variation over the entire range of NaCl concentration that had been measured, with an average agreement within 1.7%. The results shown in Fig. 1 provide us with confidence to proceed with seawater.

For seawater, we used Eq. (9) to estimate the scattering due to concentration fluctuation. Fig. 3 shows the spectral scattering estimated for  $S = 38.4\text{‰}$ , and  $T_c = 20^\circ\text{C}$  and their comparison with the measurements by Morel [5, 6]. Also compared in Fig. 3 are Morel's theoretical estimates of scattering for seawater [Table 4 in 13], which has been widely used [e.g., 11]. The theoretical prediction of our model agrees with Morel's measurements within 1.0%, well within the experimental error of 2%. It was recently suggested [8, 9] that Morel's theoretical estimates (the green curve) might be high; and our theoretical calculation (red curve) confirmed the argument.

The scattering of seawater as a function of salinity calculated at 546 nm and  $20^\circ\text{C}$  are shown in Fig. 4. Clearly, the variation of scattering with the salinity is a combination of two factors: decreasing contribution due to density fluctuation (Eq. (2)) and increasing contribution due to concentration fluctuation (Eq. (9)). The effect of sea salts on the density term of scattering was briefly discussed by Morel [13], who suggested that the effect might be small due to contradictory influence of sea salts on  $\beta_T$  (decreasing with  $S$ ) and on  $n$  and  $\rho$  (both increasing with  $S$ ). Our estimate (blue line in Fig. 4) confirms these early analyses and shows that the density term decreases by  $\sim 2.6\%$  as  $S$  increases from 0 to  $40\text{‰}$ . Given the high precisions associated with the estimates of the parameters used in calculating the density contribution (Eq. (2) and Table 1), the magnitude of variation of 2.6%, though small, is statistically significant.

As can be expected, the scattering due to concentration fluctuation (dashed blue line in Fig. 4) increases with the salinity. Because of the dominant role of the term  $S$  in Eq. (9), the variation is primarily linear with small adjustments resulting from variations of  $\rho$  and  $\partial \ln a_0 / \partial S$  with  $S$ .



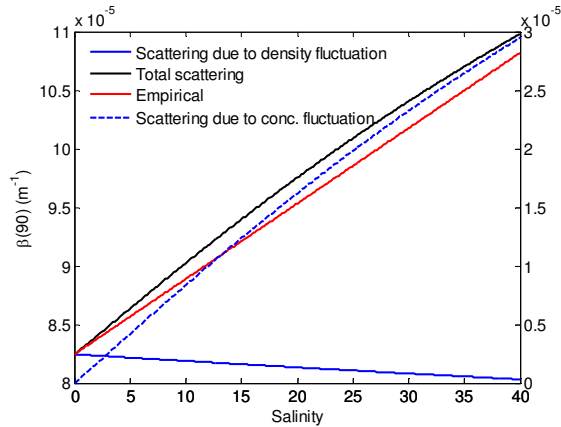


Fig. 4. Scattering of seawater due to density fluctuation (blue line), due to concentration fluctuation (blue dashed line and right Y-axis) and their total are estimated for  $\lambda = 546$  nm and  $T_c = 20^\circ\text{C}$  as a function of salinity. The empirical variation estimated using Eq. (3) is shown as red.

The estimates based on the empirical model of Eq. (3) with  $S_0=38.4$  are also shown in Fig. 4 (red line). The comparison between the theoretical and empirical estimates suggests that the linear empirical model would underestimate the seawater scattering by an average of 2% for  $S$  up to 40‰ assuming the values for pure water are estimated correctly.

The minimum scattering occurs at  $26^\circ\text{C}$ , which is the same as that for pure water. And the range of variation with temperature increases slightly for seawater, 5.5% vs. 3.7% for pure water for  $T_c$  from 0 to  $26^\circ\text{C}$ . Also, sea salts have a weak effect on the spectral dependence of scattering. With anchor wavelength  $\lambda_0$  at 450 nm, the slope  $s$  as in  $(\lambda/\lambda_0)^s$  determined from non-linear fitting varies from -4.286 to -4.306 for  $S$  from 0 to 40‰. These values are very close to Morel's estimate of -4.32. We used  $s = -4.30$ , roughly the mean, in Fig. 1 to scale the scattering of NaCl solution from 546 nm to 589 nm.

Equation (9) was derived theoretically from thermodynamic principles, therefore its applicability is only limited by the ranges of validity of its parameters that are determined empirically (Table 1). The empirical model for the refractive index, though originally developed for the visible region [18], has been shown to fit the available data well over an extended range of 200 – 1100 nm [35]. The valid range for the temperature is 0 –  $30^\circ\text{C}$  and for the salinity 0 – 40‰. While these ranges cover most of oceanic and coastal waters, the formulae for density, refractive index, activity, and isothermal compressibility may not apply for inland seas, whose salt components might have different molar ratios among themselves from those for seawater. Also extrapolation beyond these applicable ranges should be verified with independent measurements.

As shown in Table 1, the relative errors in modeling the parameters used to estimate the seawater scattering are very small. We estimated that the relative error in the model itself is only 0.04%, which is primarily due to the term,  $\partial \ln a_0 / \partial S$  in Eq. (9). Therefore the accuracy of the model for the concentration fluctuation part is primarily determined by the assumption that we have made regarding the thermodynamic behavior of the dissolved components of sea salts – they maintain the relative molar ratio with each other during the fluctuation. The close agreements in scattering between the theoretical predictions by this study and the measurements by Morel [5, 6] for NaCl solution and seawater as shown in Figs. 1 and 3, respectively, do provide justification. Recently, Lund et al. [30] estimated the activity coefficients in seawater using Monte Carlo simulations based on electric neutrality, which is similar to our assumption. They showed that their results are in excellent agreement with the experimental determinations and the estimates based on the Pitzer model. This also partly supports the validity of our assumption. However, if the assumption does not stand, we think

it would lead to an overestimate of the contribution by sea salts, because if only part of the ions fluctuate while the rest remains still, the magnitude of concentration change would be smaller.

The other major source of uncertainty is the value adopted for the depolarization ratio. Sea salts are expected to modify the value of depolarization ratio of water with two contradictory effects: reducing  $\delta$  because ions are isotropic and enhancing  $\delta$  because their electrostatic field causes increased anisotropy [13, 17]. Both of the effects have been observed; for example, Pethica and Smart [19] measured the variations of  $\delta$  with concentration that was increasing in a  $\text{KNO}_3$  solution but decreasing in a  $\text{KCl}$  solution. We do not know yet how  $\delta$  would vary with salinity and in this study we have assumed that  $\delta$  remains unchanged.

In our previous study [2], we analyzed the effect of  $\delta$  on the scattering by pure water and the results suggested that within the range of values of  $\delta$  from 0.039 to 0.051 that have been measured [4], the model we proposed converges with the measurements by Morel [5, 6] from -0.7% to 2%. Results in Fig. 3 were calculated with  $\delta = 0.039$  and the average difference is 1%; if  $\delta = 0.051$ , the difference would be 3.7%. Given the experimental error of 2% reported for the measurements by Morel and assuming the same values of  $\delta$  apply to seawater, the model developed seems to overestimate a little. This is consistent with our estimate of possible errors introduced by the assumption discussed above. However, in order to further constrain the uncertainty in seawater scattering, we need to improve our understanding of the effect of sea salts on the depolarization ratio.

#### 4. Conclusions

We estimated the effect of sea salts on the scattering by seawater by developing a model calculating the scattering due to concentration fluctuation as a function of salinity. The results agreed with Morel's measurements with an average difference of 1%, which is within his experimental error of 2%. While in general, the scattering by seawater increases with salinity, the linear adjustment frequently used will cause an underestimate by 2% on average. The underlying assumption of the model was that relative molar ratios of components of dissolved sea salts remain constant with each other at microscopic scales during concentration fluctuation. As we have discussed and shown by the results, we think the impacts of the assumption are limited. Another factor contributing to the improved modeling is the recent availability of high quality estimates (either through measurement or modeling) of the key thermodynamic parameters, such as the activity and partial molar volume of seawater. To further test its applicability, the Matlab code of the model developed in this study is available to the community ([http://www.und.edu/instruct/zhang/programs/betasw\\_ZHH2009.m](http://www.und.edu/instruct/zhang/programs/betasw_ZHH2009.m)).

#### Appendix

According to Einstein-Smoluchowski theory, the scattering by a solution that is due to concentration fluctuation is

$$\beta_c(90) = \frac{\pi^2}{2\lambda^4} \Delta V \overline{\Delta\epsilon^2} f(\delta) \quad (\text{A1})$$

where  $\overline{\Delta\epsilon^2}$  represents the fluctuations of dielectric constant due to concentration at a constant temperature and within a constant volume of  $\Delta V$ , which is small as compared to the wavelength  $\lambda$  and yet large enough for the laws of statistical thermodynamics to apply. The concentration of sea salts,  $c$ , within this small volume of  $\Delta V$  can be expressed as,

$$c = \frac{m_{ss} \sum f_i M_i}{\Delta V} \quad (\text{A2})$$

where  $m$  denotes the total number of moles of electrolytes,  $M$  the molecular weight, and  $f$  the fractional abundance of different electrolytes in mole/mole ( $\sum f_i = 1$ ). For the subscripts in Eq. (A2) and hereafter,  $ss$  denotes the quantities associated with sea salts or electrolytes in general, and  $i$  for one of the components of sea salts. Because the composition of sea salts and their concentration relative to each others are approximately constant over the global oceans, the parameters  $f_i$  as well as the summation  $\sum f_i M_i$  in Eq. (A2) can be assume to be constant. Let  $M_{ss}$  denote  $\sum f_i M_i$ . If we further assume that on a microscopic scale,  $f_i$  also remains constant with each other during fluctuation, then the concentration fluctuation,  $dc$ ,

$$dc = \frac{dm_{ss} M_{ss}}{\Delta V}. \quad (\text{A3})$$

The assumption in Jonasz and Fournier [16] that all the sea salts are merged into one hypothetical compound can also lead to Eq. (A3). With this, the collective variation of dielectric constant due to sea salts can be written as:

$$\overline{\Delta \varepsilon^2} = \left( \frac{\partial \varepsilon}{\partial c} \right)^2 \overline{\Delta c^2}. \quad (\text{A4})$$

The concentration fluctuation,  $\overline{\Delta c^2}$ , results from changes in the mixing ratio of pure water and sea salts within a small volume of  $\Delta V$  [1], while the total mass and hence the density remains constant. This ensures that fluctuations due to density and concentration are independent to each other. Thermodynamically,

$$\overline{\Delta c^2} = \frac{kT}{(\partial^2 A / \partial c^2)_{T,V}} \quad (\text{A5})$$

where  $A$  is the Helmholtz free energy [36]. The change in Helmholtz free energy associated with the concentration change at constant temperature and volume is given by,

$$dA = \mu_0 dm_0 + dm_{ss} \sum_i f_i \mu_i \quad (\text{A6})$$

where  $\mu$  denotes the chemical potential. Within a small volume,  $\Delta V$ , the number of moles of pure water and sea salts are related by,

$$\Delta V = m_0 \overline{V}_0 + m_{ss} \sum_i f_i \overline{V}_i \quad (\text{A7})$$

where  $\overline{V}$  denotes the partial molar volumes. Since  $\Delta V$  is held as a constant, we have from Eq. (A7) that

$$dm_0 = - \frac{\sum_i f_i \overline{V}_i}{\overline{V}_0} dm_{ss}. \quad (\text{A8})$$

The partial molar volumes depend on the concentration too, but the fluctuations that we are concerned with here are too small to be important. For example, from Eq. (8) we estimated that  $\Delta \overline{V}_0 / \overline{V}_0 \approx 2.4 \times 10^{-3} \Delta m_{ss} / m_{ss}$  and  $\Delta \overline{V}_i / \overline{V}_i \approx 1.3 \times 10^{-6} \Delta m_{ss} / m_{ss}$ . Therefore we can safely assume that the partial molar volumes are constant during the concentration fluctuations ( $\Delta m_{ss}$ ). Combining Eqs. (A6) and (A8), we obtain,

$$dA = (\sum f_i \mu_i - \frac{\sum f_i \bar{V}_i}{V_0} \mu_0) dm_{ss}. \quad (\text{A9})$$

From Eq. (A9) we have  $\partial A/\partial m_{ss}$  and from Eq. (A3) we have  $\partial c/\partial m_{ss}$ ; combining these two, we obtain,

$$\left(\frac{\partial A}{\partial c}\right)_{T,V} = (\sum f_i \mu_i - \frac{\sum f_i \bar{V}_i}{V_0} \mu_0) \frac{\Delta V}{M_{ss}} \quad (\text{A10})$$

Differentiating Eq. (A10) with respect to  $c$ , we have

$$\left(\frac{\partial^2 A}{\partial c^2}\right)_{T,V} = (\sum f_i \frac{\partial \mu_i}{\partial c} - \frac{\sum f_i \bar{V}_i}{V_0} \frac{\partial \mu_0}{\partial c}) \frac{\Delta V}{M_{ss}} \quad (\text{A11})$$

The differentials of chemical potentials for the components in a system are related by the Gibbs-Duhem equation,

$$m_0 d\mu_0 + m_{ss} \sum f_i d\mu_i = 0 \quad (\text{A12})$$

Substituting  $\sum f_i d\mu_i$  in Eq. (A11) with that in Eq. (A12), Eq. (A11) becomes

$$\left(\frac{\partial^2 A}{\partial c^2}\right)_{T,V} = -\frac{\Delta V}{V_0} \left(\frac{m_0 \bar{V}_0 + m_{ss} \sum f_i \bar{V}_i}{m_{ss} M_{ss}}\right) \left(\frac{\partial \mu_0}{\partial c}\right)_{T,V}. \quad (\text{A13})$$

Recalling Eq. (A7) for  $\Delta V$  and Eq. (A2) for  $c$ , the second term of Eq. (A13) is effectively  $1/c$ , which leads to a simplification of Eq. (A13) to

$$\left(\frac{\partial^2 A}{\partial c^2}\right)_{T,V} = -\frac{\Delta V}{c V_0} \left(\frac{\partial \mu_0}{\partial c}\right)_{T,V}. \quad (\text{A14})$$

By definition, chemical potential and activity of a species are related,

$$\mu = \mu^0 + RT \ln a \quad (\text{A15})$$

where  $\mu^0$  is the chemical potential of the species in a standard state and  $R$  is the gas constant. For seawater, the state can be the temperature and pressure under which the scattering is being measured or calculated. Differentiating Eq. (A15) with respect to the concentration of sea salts and substituting the result into Eq. (A14), we obtain,

$$\left(\frac{\partial^2 A}{\partial c^2}\right)_{T,V} = -RT \frac{\Delta V}{c V_0} \left(\frac{\partial \ln a_0}{\partial c}\right)_{T,V} \quad (\text{A16})$$

Though not appearing in Eqs. (A14) and (A16) explicitly, the effects of sea salts were carried through the changes in the chemical potential and activity of the solvent as the concentration fluctuates. Combination of Eqs. (A16), (A5), (A4) and (A1) leads to Eq. (5), which was originally developed for a two-component solution. We have shown that it can be used for seawater too, under the assumption that sea salts would fluctuate in synchronization with each other such that their molar ratios among each other remain unchanged.

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