Scattering by solutions of major sea salts

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Abstract: Increased scattering by seawater relative to that by pure water is primarily due to additional fluctuation of the refractive index contributed by sea salts. Salts with different ionic weight and sizes, while barely affecting the scattering that is due to density fluctuations, have a significant effect on the scattering that is due to concentration fluctuations. And this explains the major differences of their total scattering that would be observed. Scattering by solutions of NaCl, the major sea salt, is consistently about 6.7% and 4% lower than seawater of the same mass concentration and of the same refractive index, respectively. Because of ionic interactions, the molecular scattering does not follow the simple addition rule that applies to bulk inherent optical properties, with the total less than the summation of the parts. The possible values of scattering by waters of, such as, Dead Sea or Orca Basin, which have different salt composition from seawater, are discussed.

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

References and links


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26 October 2009 / Vol. 17, No. 22 / OPTICS EXPRESS 19580
1. Introduction

Increased scattering by seawater relative to that by pure water is primarily due to additional fluctuation of the refractive index contributed by sea salts. The optical properties of solutions of sodium chloride (NaCl), the dominant component of sea salts, have been studied in detail. Morel [1,2] measured the scattering at 366 and 546 nm by an NaCl solution at various concentrations up to 100 g/l. In general, the scattering was found to increase with concentration, but the increase was slower at higher concentrations. A similar non-linear variation was also found by Sullivan and Twardowski (unpubl. data). The spectral dependence of pure water absorption on dissolved salt concentration was measured by Pegau et al. [3] and Sullivan et al. [4]. Both studies found that presence of NaCl would introduce negligible absorption in the visible, especially for wavelengths < 600 nm. Ravisankar et al. [5] reported that variations in NaCl concentration did not have a significant effect on the attenuation coefficient.

In addition, NaCl solutions have often been used as a proxy for pure seawater in calibrations of field radiometers [e.g., 3,4] because of extreme difficulty in removing dissolved organic matter from natural seawater. A theoretical model for the scattering by NaCl solution is required for both interpreting laboratory measurements and developing calibration parameters.

Knowledge of the scattering by individual salt solutions are not only important in themselves, but also critical in improving our understanding of the scattering by isolated water bodies, whose composition of salts are often different from that of seawater. For example, while NaCl accounts for ~77% of sea salts in the ocean, 50% of salts by mass in the Dead Sea is MgCl₂ due to lower precipitation concentrations of NaCl and other salts [6]. Also, in hot arid areas such as Orca Basin or Dead Sea, slow evaporation of seawater would drive almost all SO₄²⁻ ions out of water, precipitating as gypsum (CaSO₄•2H₂O) and leaving Cl⁻ as (almost) the sole anion [7].

The general theory of scattering by an electrolyte solution is well established [8,9], however its application has been impeded by a lack of data on the thermodynamic parameters required to drive the model. Recently, Zhang and his associates [10–12] refined the theory based on the key thermodynamic parameters that have been measured with high quality, and their models agree with the measurements [1,2] within the experimental errors. This improved modeling capability allows us to re-evaluate scattering by individual sea salt solutions in an attempt to gain a better understanding of scattering by seawater and other natural water bodies.

2. Scattering by sea salt solutions

From the fluctuation theory [13], the scattering coefficient, b (m⁻¹), by a pure solution, is due to two independent contributions:

\[ b = b_d + b_c \]

where \( b_d \) and \( b_c \) are the scattering due to density and concentration (mixing ratio) fluctuations, respectively. Following Zhang and Hu [10] and Zhang et al. [11], the terms \( b_d \) and \( b_c \) can be further expressed as:

\[ b_d = \frac{8\pi^3}{\lambda^4} \left( \frac{\partial n}{\partial \rho} \right)^2 kT \beta_{\lambda} h(\delta) \]

where \( \beta_{\lambda} \) is the thermal expansion coefficient, \( h(\delta) \) is a function of the concentration fluctuation \( \delta \), and \( \rho \) is the density of the solution.

and

\[ b_c = \frac{8\pi^3}{\lambda^2 N_A} \left( \frac{\partial n^2}{\partial S} \right)^2 M_w \frac{S}{\rho - \partial \ln a_w / \partial S} h(\delta). \]  

respectively, where \( \lambda \) is the wavelength, \( k \) the Boltzmann constant, \( N_A \) the Avogadro number, \( \rho, n, T, \beta_T, S \) and \( \delta \) are the density, the refractive index in vacuum, the absolute temperature, the isothermal compressibility, the salt concentration and the depolarization ratio of the solution, respectively, and \( a_w \) and \( M_w \) are the activity and molecular weight of water in the solution respectively. Also \( h(\delta) = (2 + \delta)/(6 - 7\delta) \).

The major ions in seawater include Na\(^+\), Mg\(^{2+}\), Cl\(^-\), and SO\(_4^{2-}\), altogether accounting for > 96% of the total mass of sea salts [7]. Therefore, the individual salt solutions being considered in this study are: NaCl, MgCl\(_2\), Na\(_2\)SO\(_4\), and MgSO\(_4\). The thermodynamic parameters in Eqs. (2) and (3) are fitted to a general Debye-Hückel form as a function of salt concentration (\( M \)) in molality,

\[ X = a_0 + a_1 M + a_2 M^{1.5} + a_3 M^2. \]  

The coefficients \( a_{0,3} \) are derived, respectively, from Handbook of Physics and Chemistry [14] for \( X = \rho \) or \( n \), from Millero et al. [15] for \( X = \beta_T \), and from Pitzer and Mayorga [16] for \( X = a_w \).

![Fig. 1. Scattering by NaCl solution at 366 and 546 nm and 20°C calculated using Eq. (1) is compared with the measurements by Morel [1,2]. The theoretical values at 589 nm, where the physical constants of the model were empirically determined, were scaled to 366 and 546 nm, respectively, following the power-law of a slope of 4.23, a value that was determined from Morel’s measurements.](image)

3. Results and discussion

The estimates of scattering by an NaCl solution at 366 and 546 nm were compared with the measurements by Morel [1,2] and the results are shown in Fig. 1. A value of 0.039 for the depolarization ratio parameter, \( \delta \) [17] was used for Fig. 1 and the rest of the calculations. The calculations agree with the measurements within the experimental errors of 2% (1.7% for the comparison at 366 nm and 0.9% for that at 546 nm). Unfortunately, there have been no reports on scattering by MgCl\(_2\), Na\(_2\)SO\(_4\), or MgSO\(_4\) solutions. However, given the close agreement between the theory and the experiment for NaCl solutions, we assume that the model (Eqs. (2) and (3)) and the methodology in deriving its thermodynamic parameters (Eq. (4)) would apply to the other salt solutions as well.
The scattering as a function of concentration calculated for the four solutions using Eqs. (1)-(3) and for pure seawater using the model of Zhang and Hu [12] are shown in Fig. 2-(a) for their partitions into density and concentration fluctuations components and in Fig. 2-(b) for their total. Scattering due to density fluctuations (Eq. (2)) is about the same for different salt solutions and seawater, and they all decrease slightly with concentration. The differences in the total scattering coefficients for different solutions as seen in Fig. 2-(b) are primarily caused by the differences in concentration fluctuations (Eq. (3)) as introduced by the presence of salts. For simple non-electrolyte solutions, the intensity of scattering is related to and has been used to determine the molecular weight of solute [18]. While for an electrolyte solution, strictly speaking, this relationship no longer applies [11], Fig. 2-(b) suggests that the relative magnitude of scattering still roughly follows the order of mean ion weights, which are estimated to be 29.2, 31.7, 60.2, and 47.3 for NaCl, MgCl$_2$, MgSO$_4$, and Na$_2$SO$_4$, respectively. The mean ion weight for seawater is 31.33 [7].

In water, the electrostatic field of ions forces the neighboring water dipoles to orient their appropriated charged ends toward the ions, forming scattering centers whose mean scattering cross section depends on the size distribution of ionic radii. The ionic radii are about 0.097, 0.07, 0.180 and 0.242 nm for Na$^+$, Mg$^{2+}$, Cl$^-$, and SO$_4^{2-}$, respectively [19], which lead to approximately the same mean ionic radii of 0.143 nm for both MgCl$_2$ (1 Mg$^{2+}$ + 2 Cl$^-$) and Na$_2$SO$_4$ (2Na$^+$ + SO$_4^{2-}$) solutions. This may explain the relatively close values in scattering between MgCl$_2$ and Na$_2$SO$_4$ solutions as seen in Fig. 2-(b). The significantly higher values of scattering for MgSO$_4$ solutions are also due to ion pairing; approximately 11% of magnesium exists as MgSO$_4$ in water [7], which leads to bigger scattering cross sections.

The scattering increases with the concentration of a solution, simple or complex, in a non-linear manner. The linear models based on the ideal-solution assumption [e.g., 20] or based on interpolating a couple of experimental values [e.g., 21] will likely under- and overestimate the scattering at lower and higher concentrations, respectively, with increasingly larger errors towards higher concentrations [12]. Ravisankar et al. [5] measured the spectral attenuation coefficients of NaCl, MgCl$_2$, and Na$_2$SO$_4$ solutions. Since salts have negligible absorption in the visible [4], by subtracting the absorption coefficient of pure water [22] from their measurements, we obtained scattering coefficients at 589 nm of 0.0251, 0.0378, and $-0.0165 \, \text{m}^{-1}$ for the NaCl solution at concentrations of 9.9, 19.8 and 29.4 g kg$^{-1}$, respectively; 0.0044, 0.0472, 0.0616 m$^{-1}$ for the MgCl$_2$ solution at concentrations of 5.0, 14.8, and 23.4 g kg$^{-1}$, respectively; and 0.0259 and 0.022 m$^{-1}$ for the Na$_2$SO$_4$ solution at concentrations of 5.0 and 34.5 g kg$^{-1}$, respectively. In general, their values are an order of magnitude higher than those in Fig. 2-(b) even though the general patterns of variation for MgCl$_2$ are similar. The
disagreement, we believe, is mostly due to the relatively large uncertainty associated with their measurements. For example, the negative scattering coefficient derived above for the NaCl solution of 29.4 g kg$^{-1}$ (30 g/l) was because that the measured attenuation coefficient of 0.1134 m$^{-1}$ at 589 nm is 15% lower than the attenuation coefficient of pure water at the same wavelength (0.1299 m$^{-1}$). An experiment with this level of uncertainty would not be able to detect the magnitude of variations of scattering, which is on the order of $10^{-3}$ to $10^{-2}$ m$^{-1}$ depending on the wavelength.

As NaCl is the dominant salt of seawater, the variations of scattering with salt concentrations are similar between the two solutions. However, because of the presence of other heavier and bigger salts, the scattering by seawater is consistently higher than that by NaCl solutions at the same concentration. For $S > 20$ g kg$^{-1}$, the scattering by seawater is on average 6.7% higher than NaCl solutions. Sometimes the concentration of organic free NaCl solutions is adjusted so that the refractive index of the NaCl solutions matches that of seawater. Our calculations showed that for the refractive index varying from 1.333 to 1.355 ($S$ from 0 to 120 g kg$^{-1}$), the total scattering coefficient for the NaCl solution is about 4% lower. Therefore, when NaCl solutions are used as a proxy of seawater in the calibration of field instruments [e.g., 3,4], this difference in scattering needs to be accounted for.

Since seawater or other natural water bodies are a mixture of different salts, it would be of interest to see whether the scattering by a solution of a mixture of different salts can be reproduced by the scattering of its individual salt solutions. For seawater, NaCl, MgCl$\text{}_2$, MgSO$\text{}_4$, and Na$_2$SO$\text{}_4$ account for 77.6%, 10.89%, 4.73%, and 2.46%, respectively, of the total salts (~96% altogether). The scattering by these four individual salt solutions are calculated at their respective fractional concentrations and their total is compared with the scattering by seawater in Fig. 3. Apparently, the scattering by an electrolyte solution of multiple salts cannot be reproduced by simply summing up the contributions by the individual salt solutions, even though the errors are small when $S < 40$ g kg$^{-1}$. However, this is not unexpected. Zhang et al. [11] discussed that ions in seawater or other natural water bodies are paired through covalent bond, electrostatic bond, or solvent-shared electrostatic bond (separated by one or more water molecules) [23]. Electrostatic interaction among ions impose some degree of order over random thermal motion [24], and therefore a mixture of salts with more ionic interaction would exert further restrictions on the concentration fluctuations than a simple salt solution. In

![Fig. 3. Scattering at 589 nm and 20°C by four major sea salt solutions are calculated as a function of their respective fractional concentrations at a given salinity. The sum of the individual scattering estimates is compared with the theoretical estimate of scattering by seawater.](image)
other words, as far as molecular scattering by a solution is concerned, the whole is less than the sum of parts.

Despite complex ion-ion and ion-water interactions, we can still constrain the magnitudes of scattering if the fractional concentrations of the dominant salts are known. Based on Fig. 2-(b), we expect that molecular scattering by Dead Sea water should be higher than that by seawater for two reasons. First, the salinity is much higher in Dead Sea, close to saturation (> 250 g kg\(^{-1}\)). Second, while both NaCl and MgCl\(_2\) are still the dominant salts in Dead Sea, their proportions are about 50%:30% \([6]\) vs. 77%:11% for the ocean. Since at the same concentrations, a MgCl\(_2\) solution scatters more than an NaCl solution (Fig. 2-(b)), we would expect that the total molecular scattering of Dead Sea water would also be higher, but will still be less than that by pure MgCl\(_2\) solutions. For waters of the Orca Basin, with strong evaporation, NaCl becomes the predominant salt, accounting for > 90% of the total salt mass \([7]\). The scattering in these waters will be even closer to that of an NaCl solution than seawater.

Our model is valid at 589 nm, where most of empirical constants (Eq. (4)) are measured or determined. Based on Morel’s measurements at two wavelengths of 366 and 546 nm (Fig. 1), the mean power-law slope for NaCl solutions is \(\approx -4.23\). The slope for seawater varies from \(\approx -4.28\) to \(\approx -4.30\) depending on salinity \([11,12]\). We do not expect the spectral variation of scattering by other individual salt solutions to be significantly different from these values.

4. Conclusions

Scattering by individual solutions of major sea salts were estimated. Salts with different ionic weight and sizes, while barely affecting the scattering that is due to density fluctuations, have a significant effect on the scattering that is due to concentration fluctuations of the refractive index. This explains the major differences of their total scattering that would be observed. Solutions of NaCl, the major sea salt, exhibit a consistently lower scattering of about 6.7% than seawater at the same concentrations. Because of ionic interactions, the molecular scattering does not follow the simple addition rule that applies to bulk inherent optical properties, with the total less than the summation of the parts. However, knowledge of scattering by individual salt solutions will still be helpful in constraining the scattering by other natural water bodies with a different salt composition from seawater.

Acknowledgements

The work was done while LH is a visiting researcher at the University of North Dakota supported by grants from NASA and USDA. Part of funding for XZ was provided by National Natural Science Foundation of China project NSFC-60638020 and ONR. Contributions from MST and JMS were supported by Office of Naval Research contracts N0001406C0027 and NASA contracts NNX06AH32G and NNX06AH86G. We thank the comments by the anonymous reviewer.