Light-scattering characteristics of hydrated ions in dilute solutions of major sea salts

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ABSTRACT

The major ions in seawater include Na^+, Mg^{2+}, Cl^-, Ca^{2+}, and K^+, altogether accounting for >96% of the total mass of sea salts. The radii of ions in solution depend on the number of the solvent molecules in their solvation shells, and so would have an influence on the light-scattering of the aqueous solution. Taking in to account density fluctuation theory of pure water and Rayleigh scattering of hydrated ions, a theoretical model was developed estimating the light-scattering characteristics of the dilute ionic aqueous solution. The results show that there is a decreasing contribution due to density fluctuation, in the same salinity of solution, the most contribution to scattering due to density fluctuation is $CaCl_2$ solution and $MgCl_2 > KCl > NaCl$. There is an increasing contribution due to hydrated ions for the light scattering. For each kind of hydrated ion, the contribution is $Cl^- > Mg^{2+} > K^+ > Ca^{2+} > Na^+$, and for each kind of solution, the contribution is $MgCl_2 > CaCl_2 > NaCl > KCl$. Comparing the two contribution for the light scattering in one solution, we can get the latter effect dominating.

1. 1 Introduction

Scattering by pure water is the result of fluctuations of molecule number density resulting in changes in refractive index and is described by the Einstein–Smoluchowski theory of scattering [1]. This kind of scattering was theoretical described e.g. By Mobley [2], Morel [3], and Zhang and Hu [4]. The fluctuation are dependent on density and temperature, where the effect of temperature is <1% of that of density (not considering the effect of temperature on density).

In dilute sea water an additional scattering is caused by electrostriction of hydrated ions, which on the other side influences the total scattering. It describes the concentration dependence of the scattering coefficients and the concentration dependence of the number of water molecules hydrating the ions and of the radius of hydrated ions. The geometric arrangement of the water molecules around the ions in a first and possibly a second hydration shell, they have little bearing on the strength of the association of the ions with the water molecules surrounding them [8]. Total scattering by sea water is the sum of scattering by density fluctuations and electrostriction effect and is, hence, a linear function of the main salt ions. Empirical studies on scattering by sea water are reviewed by Morel [3] with those of Morel [5,6] being widely accepted. The theoretical approaches for its calculation are recently reviewed in Zhang and Hu [7], in which they use the fluctuation theory [1].

2. Ionic hydration

There were some experimental evidences for one or two hydration shells formed around ions [9–12]. The ions are sources of extremely high electric fields, up to about 10^{11} V/m at the distances of the first hydration shells, where the density of water placed in electric fields of strengths exceeding 10^{10} V/m has been increased in relation with X-ray diffraction experiments [13]. The density of the first hydration shells of ions were calculated on the basis of an electrostatic and thermodynamics approach by Ferchmin [14]. The electrostriction around a given ion in the hydration shells and the concentration dependence of ionic hydration numbers in aqueous electrolyte solution were evaluated by Marcus [8,15].

It was assumed that under the conditions of infinite dilution an ion is surrounded by water in its hydration shells and by bulk water having the properties of pure water beyond these shells, but the region around a given ion is not affected by any other ions, as shown in Fig. 1. The values of the local density ρ_i [13] and the radii

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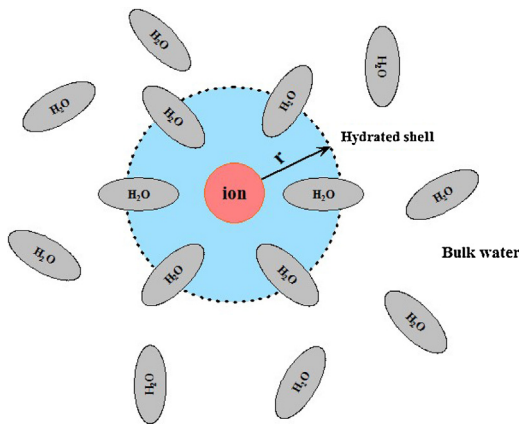E-mail address: yufengp@htu.cn (Y. Peng).

Fig. 1. Diagram for ionic hydration shell in aqueous electrolyte solution.

Table 1
Properties of the first hydration shells of major sea salt ions in the aqueous solution.

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-
Radii r_i (Å)	3.58	3.31	4.28	4.12	3.32
Mass density ρ_i (g/cm^3)	1.0	1.0	1.8	1.35	1.0
Coordination number h	5.9	2.46	13	8.5	1.5

Table 2
The polarizability of particles.

Particle	Ref.	Polarizability α (Å^3)
Water	[23]	1.444
Cl^-	[24]	0.010
Na^+	[25]	0.179
Mg^{2+}		0.094
K^+		0.839
Ca^{2+}		0.472

r_i of the first hydration shells of ions (Na^+, Mg^{2+}, Cl^-, Ca^{2+}, and K^+) [30] are given in Table 1.

The numbers of water molecules in the first shell (coordination numbers h) were given by [14]

$$h = \frac{\rho_i v_i}{M} \qquad (1)$$

where v_i represents the average volume of the first hydration shell, M the mass of a water molecule ($M = 3 \times 10^{-23}$ g), and ρ_i the water density in the field of the ion within its first shell.

Theoretically, the electrostriction of the solvent around the ions of an electrolyte necessarily leads to hydration numbers h that decrease with increasing electrolyte concentrations in dilute solutions [8]. Actually, as the solution concentration increases beyond dilute solutions, ions cannot maintain intact the hydration spheres which they have in dilute solutions and the values of the hydration numbers h should diminish once the hydrated ions are in contact.

Under the condition of infinite dilutions, the interactions between the ions in the aqueous solution can be neglected. Water will be treated as a two-phase system. One of those phases is inside the electric field of the ion, whereas the other is outside this field. The static dielectric constant of ε_s, from the molecular properties of the medium can be obtained by calculating the polarization P, which is the dipole moment per unit volume of the dielectric medium. This polarization is the sum of two types: (a) distortion polarization, which is due to distortion of electronic distributions within atoms and of atomic configurations within molecules. The distortion polarization occurs with extreme rapidity, even in fields alternating with the frequency of light-wave. And (b) orientation-polarization, which is due to the orientation of

permanent molecular dipoles under the field. It involves the rotation of molecules, a slower process and is dependent of temperature.

For the case of the distortion-polarization, the dielectric constant ε_a can be given by Clausius–Mossotti formula [16], which it must be emphasized holds only for non-polar molecules in the absence of molecular inactions:

$$\frac{\varepsilon_\alpha - 1}{\varepsilon_\alpha + 2} = \frac{4\pi N_0}{3}\alpha \qquad (2)$$

where α is the molecular polarizability, which is the time-average dipole moment induced in the molecule by a field of unit intensity. N_0 denotes the molecular numbers in unit volume (molecules/cm^3).

In order to obtain the static electrical permittivity (ε_n) of water close to an ion, we consider infinite dilutions, which means that in an aqueous solution the effects of other ions on water molecules close to a given ion are neglected. And thus it enables one to calculate ε_n as a function of the distance from an ion [17]. The relation between the permittivity ε_n due to orientation-polarization and the local electronic filed strength is, according to the Onsager local field model, expressed as [14]:

$$\frac{(\varepsilon_n - n^2)}{x^2 \varepsilon_n NB} = \langle \cos\theta \rangle \qquad (3)$$

where

$$\langle \cos\theta \rangle = \tanh\left(\frac{A}{x^2(\varepsilon_n + n^2/2)}\right)$$

$x = r|Z|^{-1/2}$, $A = \frac{\mu e(n^2+2)}{8\pi k_B T\varepsilon_0}$ and $B = \frac{4\pi\mu(n^2+2)}{3eV_m}$ here μ is the dipole moment of a water molecule, n the light refraction index. e denotes the elementary charge, ε_0 permittivity of vacuum, N number of water molecules, V_m molar volume of water, and Z ionic valence. θ is the angle between the dipole moment μ of the water molecule and the radial electric field.

3. Light scattering

The scattering of light originates from the localized fluctuations in density and electrostriction caused by microscopic inhomogeneities in refractive index (n). In dilute sea salt solutions, the scattering can be considered by two independent contributions:

$$b = b_d + b_i \qquad (4)$$

where b_d is the scattering due to density fluctuations, b_i is the scattering due to electrostriction caused by hydrated ions and it contains two parts:

$$b_i = b_c + b_a \qquad (5)$$

where b_c denotes the scattering by hydrated cation, b_a denotes the scattering by hydrated anion.

3.1. Rayleigh scattering

The major ions in seawater include Na^+, Mg^{2+}, Cl^-, Ca^{2+}, and K^+, altogether accounting for >96% of the total mass of sea salts [18]. Therefore, the individual salt solutions being considered in this study are: NaCl, MgCl$_2$, KCl, and CaCl$_2$.

In Rayleigh theory, Rayleigh considered the problem of the passage of light through a continuous medium in which particles of spherical shape are randomly distributed on the basis of the elastic theory of light, and then from the viewpoint of electromagnetic theory. These particles were assumed to be small in comparison with the wavelength of light, and to have a dielectric constant ε,