Determination of Microwave Conductivity of Electrolyte Solutions from Debye-Drude Model

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Abstract— The solvation of ions in aqueous media is a fundamental process in biology and chemistry, and the characterization of dielectric constant of aqueous electrolyte solutions at microwave frequencies composes a powerful way to understand the dynamical process in aqueous media. In this work, we have combined the classical Debye and Drude models to determine the microwave conductivity of the salt (NaCl) solution by measuring its dielectric constant. We assume the permittivity of the electrolyte solution has a compound dielectric constant model which is the sum of the Debye model contributed by the water background and the Drude model accounting for the conductive ions in the solution. As a justification of the Drude model, the damping coefficient, γ, for the conductive ions need be far greater than the angular frequency, ω. From the DC conductivity measurement, we derive the damping coefficient of the conductive ions and prove the applicability of the Drude model in our experimental microwave regime from 0.1–20 GHz.

1. INTRODUCTION

The solvation of ions in aqueous media is a fundamental process in biology and chemistry [1]. The characterization of dielectric constant of aqueous electrolyte solutions at microwave frequencies composes a powerful way to understand the dynamical process in aqueous media [2–4]. In addition, it plays an important role in investigating the interaction between electromagnetic waves and the biological tissues that have high water content and a significant concentration of ions [5, 6]. Usually, conductivity and permittivity are the most fundamental parameters in the research of electromagnetic properties of the solutions. Compared with the direct current (DC) conductivity, it is interesting to ask if the microwave conductivity of the solutions could be measured and display some difference from the DC value.

In this work, we have combined the classical Debye and Drude models to determine the microwave conductivity of the salt (NaCl) solution by measuring its dielectric constant, i.e., permittivity, in the frequency range 0.1–20 GHz. As a typical example of Debye model, the relative permittivity of pure water obeys the dispersion relationship as following:

$$\varepsilon_r^{\text{water}}(\omega) = \varepsilon_r^{\text{water}'} + j\varepsilon_r^{\text{water}''} = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{1+\omega^2\tau^2} + j\frac{(\varepsilon_s - \varepsilon_\infty)\,\omega\tau}{1+\omega^2\tau^2}, \tag{1}$$

where ε_s is the static (DC) value of the dielectric constant, ε_∞ is the optical (infinite frequency) value of the dielectric constant, and τ is relaxation time which is the inverse of water molecules' collision frequency.

The Drude model of the relative permittivity for a metallic conductor could be written as

$$\varepsilon_r^{\text{Drude}} = \varepsilon_r^{\text{Drude}'} + j\varepsilon_r^{\text{Drude}''} = \left(1 - \frac{\omega_p^2}{\omega^2+\gamma^2}\right) + j\frac{\omega_p^2}{\omega}\frac{\gamma}{\omega^2+\gamma^2}, \tag{2}$$

$$\omega_p^2 = \frac{Ne^2}{\varepsilon_0 m}, \tag{3}$$

where ω_p is the plasma oscillation frequency, N is the particle number per unit volume, e is the electronic charge, ε_0 is the permittivity of vacuum, m is the mass of the conductive particle, and γ is the damping coefficient, representing the loss of the system. Within the approximation of $\omega \ll \gamma$, Eq. (2) can be simplified to be $\varepsilon_r^{\text{Drude}} \approx j\sigma/\varepsilon_0\omega$ where $\sigma = Ne^2/m\gamma$ is the conductivity [7].

Very similar to the free electrons in metals, the ions in the electrolyte solutions are considered as free carriers,responsible for the conductivity. The big difference is the background where the free carriers are moving is water for the electrolyte solutions and is atomic lattice for the metallic conductors. In order to exclude the influence of the background, we assume that the permittivity of the electrolyte solution has a compound dielectric constant model which is the sum of the Debye model contributed by the water background and the Drude model accounting for the conductive ions in the solution.

2. EXPERIMENTS

The salt (NaCl) solutions of several mass concentrations are used in our experiments underambient temperature. The measurement of the permittivity of the salt solution is performed by using a network analyzer (Agilent N5230C) which transmits and receives the microwave signals from 0.1 to 20 GHz and a coaxial probe (Agilent 85070E) which is a good choice to measure the permittivity for liquids. Figure 1 shows the real and imaginary parts of the relative permittivity for the pure water and the NaCl electrolyte of mass concentration 6.93%.

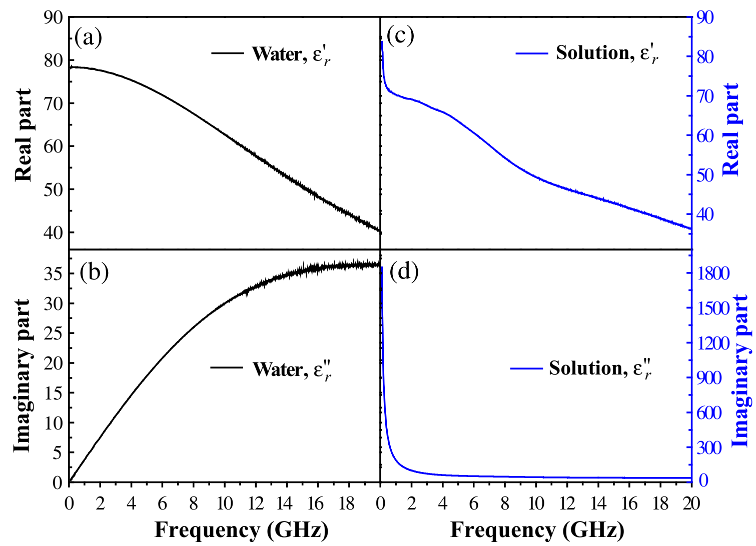

Figure 1: The measured relative permittivities of the pure water and the 6.93% salt solution. The permittivity values of the water are associated with the left axis, and those of the solution with the right axis.

3. RESULTS AND DISCUSSIONS

The contribution of Drude model from the conductive ions is calculated to be:

$$\varepsilon_r^{\text{Drude}} = \varepsilon_r^{\text{electrolyte}} - \varepsilon_r^{\text{water}} \tag{4}$$

From the simplified Drude model, we obtain the microwave conductivity $\sigma = \omega\varepsilon_0(\varepsilon_r^{\text{electrolyte}''} - \varepsilon_r^{\text{water}''})$. By this approach, we determine the microwave conductivity spectrum for various concentrated NaCl solutions, as depicted in Fig. 2. It is seen that the microwave conductivity is flat in the regime of lower frequencies and approaches to near zero at 20 GHz. This is not difficult to understand, taking into account that the conductiveanions and cations in the electrolyte are much heavier than free electrons in the metal. At lower frequencies, the movement or relaxation of the ions can respond to the microwave electric field without obvious retard, resulting in a nearly constant conductivity. However, with the increase of frequency, the relaxation of the ion could not follow the oscillating external electric field, giving rise to the obvious decrease of the conductivity.

It is also interesting to compare the conductivity at lower frequencies with the DC value which is measured by using a conductivity meter (Mettler Toledo FE30). It should note the microwave conductivity with the lowest concentration at lower frequencies matches the DC value, but there is an increasing difference between these two values as increasing the salt concentration, which is attributed to the Debye-Falkenhagen effect [8].

In the above simplified Drude model, we require the damping coefficient, γ, is far greater than the angular frequency, ω. The DC conductivity can be utilized to evaluate γ, according to the following formula

$$\sigma_{\text{DC}} = Ne^2\left(\frac{1}{m_{\text{Cl}^-}} + \frac{1}{m_{\text{Na}^+}}\right)\frac{1}{\gamma}, \tag{5}$$

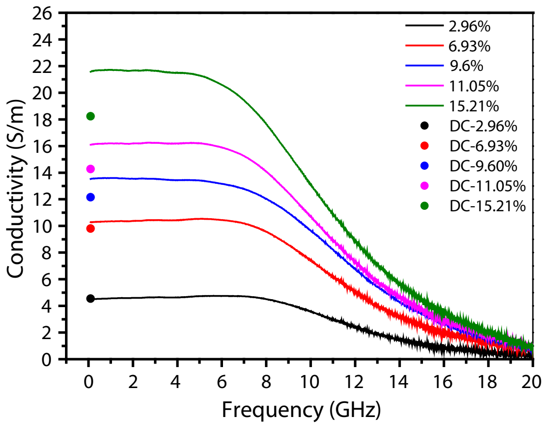

Figure 2: The microwave conductivities (solid lines) and the corresponding DC values (dots) for the five different mass concentrations of salt solution.

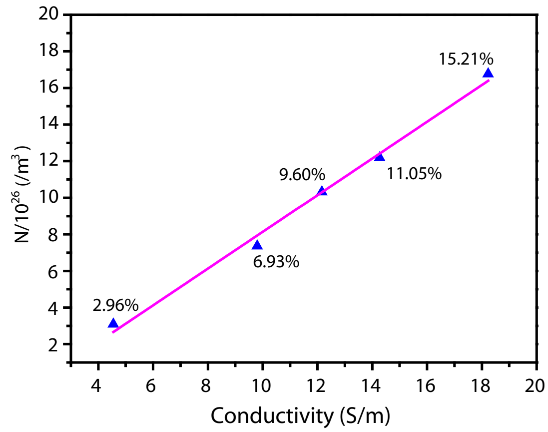

Figure 3: The N-σ_{DC} curve where the blue triangles denote the measurements and the red line is the linear fitting.

where the mass of Cl^- and Na^+ are 5.887×10^{-23} g and 3.818×10^{-23} g, respectively. Through the slope of the curve which describes the DC conductivity versus the particle number density N, we can calculate the value of damping coefficient. In Table 1, we list the unit volume particle number of ions in the solutions of different mass concentration.

Table 1: The number density of ions and the value of conductivity in the salt solutions with different mass concentration.

Sample number	Mass concentration	$N/10^{26}$ (number/m^3)	DC Conductivity (S/m)
1	2.96%	3.09	4.55
2	6.93%	6.93	9.80
3	9.60%	10.31	12.16
4	11.05%	12.18	14.27
5	15.21%	16.77	18.23

As shown in Fig. 3, we have plotted the N-σ_{DC} curve, and done the linear fitting to obtain the slope and derived the damping coefficient $\gamma = 1.1 \times 10^{14}$ Hz. Compared with the angular frequency at microwave regime, the damping coefficient γ is seen to be much greater than ω, and it proves the applicability of the simplified Drude model in our experimental microwave regime.

4. CONCLUSION

In conclusion, we have regarded the compound dielectric constant of the salt (NaCl) solution as the sum of the free ions contribution (Drude model) and the water background (Debye model). In this way, the microwave conductivity can be determined from measuring the permittivities of the electrolyte and the water. We have obtained the microwave conductivity at different concentrations in the frequency range 0.1–20 GHz. Compared with the DC measurement, we observe the increasing difference between both at lower frequency with increasing the concentration. We also calculate the damping coefficient for the conductive ions and prove that in our experimental regime the damping coefficient, γ, is far greater than the angular frequency, ω, which means our assumption is valid.

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