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Dielectric Behavior of Suspensions of Polystyrene–Zinc Oxide Composite Microspheres

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The dielectric behavior of suspensions of polystyrene/zinc oxide (PS/ZnO) composite particles in aqueous and electrolyte solution have been investigated by dielectric relaxation spectroscopy (DRS) in the frequency range from 40 Hz to 110 MHz. Two relaxations were confirmed by means of the logarithmic derivative method in this frequency range, which turned out to be very effective in resolving overlapped relaxations. The effects of volume fraction and the electrolyte concentration of composite particles on the dielectric response of suspensions were examined in detail, respectively. According to dielectric analysis, we found an abnormal and significative phenomenon, namely, special dielectric increments, where \( \delta \varepsilon_l = (\varepsilon_l - \varepsilon_m)/\varepsilon_m \) and \( \delta \varepsilon_h = (\varepsilon_m - \varepsilon_h)/\varepsilon_m \) denoting the low- and high-frequency relaxation amplitude of suspensions of PS/ZnO particles per unit volume, respectively, were increasing with the enhancement of volume fraction \( \varepsilon_m \). On the basis of the combination of studying the dielectric parameters by fitting data with the Cole–Cole equations and phase parameters calculated by Hanai method, we proposed that except for the two distinct relaxations, the low- and high-frequency relaxations which are occurred at lower kilohertz and higher megahertz frequencies, respectively, suspensions exhibit an additional dielectric relaxation over the megahertz frequency range, here named “the third relaxation”, due to the polarization of internal double layer of the thin layer of semiconducting ZnO when an external field is applied.

1. Introduction

During the past decade, semiconductor spherical structures, including solid spheres, hollow spheres, and their core/shell structures, have been intensively studied because of their unique properties, which are ascribed from their special morphologies. As is known, such a spherical monodisperse morphology is an important factor in low light scattering at surfaces as well as high packing densities.1 Among of them, intense interest in organic–inorganic core–shell hybrid functional microspheres has been spurred on because of their potential application in optical, electrical, magnetic, and catalytic devices, by adjusting their composition, size, and structure.2–6 ZnO is not only an important semiconductor material but also plays a wide part in chemical reactions, photocatalysts, photoelectric conversion, and photoluminescent materials.7–9 Meanwhile, ZnO/organic polymer hybrid core/shell microspheres, such as ZnO/polystyrene, not only retain ZnO photoluminescent properties but also display the flexibility and easy processing of organic polymers, which gives promise to potential applications in the fields of optical materials, photoconducting devices, catalysis technique fields, and so on. Therefore, many effort has been devoted to the investigation of the synthesis of semiconductor–organic polymer core/shell structures; at the same time, the properties of the products were characterized by the method of UV–vis–NIR, IR, XRD, EDS, TG-DTA, and TEM.10–12 separately. However, compared with the significant progress in the investigation of properties of semiconductor–organic polymer core/shell structures, reports on the dielectric response of suspensions of PS/semiconductor (including PS/ZnO) core–shell microspheres are still rare, although it is important in the application field due to the electrical characteristics of the particle surface, especially in fields such as catalyst for chemical reactions and photocatalysts. Therefore, it is desirable to explore diverse strategies for the dielectric study of suspensions of semiconductor/organic polymer microspheres with promising novel properties, and methods that may be feasible, easily controllable, and easily repeatable are urgently needed.

As is known, broadband dielectric spectroscopy is a powerful experimental method to investigate the dynamical behavior of particles suspensions through the analysis of its frequency dependent dielectric response. It can be used to investigate the relaxation processes that originate from different polarization mechanisms over an extremely wide range of characteristic frequency \( (10^{10} \text{–} 10^{13}) \text{ Hz} \) and provide important and unique interfacial information. It is well-known that suspensions can be characterized by mechanisms of two typical dielectric relaxations, low-frequency dielectric relaxation and Maxwell–Wagner dielectric relaxation, both of which are sensitive to the polarization of electrical double layer of dispersed particles. The low-frequency dielectric relaxation is ascribed to the polarization of counterions in the electrical double layer, and the high-frequency relaxation is from the interfacial polarization. The low-frequency dielectric relaxation (LFDR) was first given a theoretical explanation (surface diffusion mechanism, SDM) by Schwarz13 by assuming that counterions move only along the particle surface without exchanging with the bulk electrolyte ions. Then, Dukhin and Shilov14,15 proposed that LFDR was associated with the buildup of ionic concentration gradient around particles (volume diffusion mechanism, VDM). O’Konski16 suggested that the presence of the double layer surrounding a nonconducting particle should be taken into account by introducing surface conductivity concept into the Maxwell–Wagner (MW) interfacial polarization theory. However, all these theories and assumptions were build on the basis of the polarization of charged nonconducting spherical particles; the dielectric investigation of conducting particles is so limiting that only O’Brien17 presented the dielectric response of a colloid in which the particle radius \( a \) is much greater than
the double layer thickness \( \kappa^{-1} \) and made a simple model for conducting charged particles. Then, in 1996, O’Brien\(^{20} \) developed the calculation of the field and charge distribution for an isolated spherical semiconducting particle, which showed that a suspension of semiconductors behaves as if the particles were dielectrics but with an enhanced dielectric constant. Meanwhile, the variation of permittivity with radius caused the dielectric spectrum to be quite different from that of a suspension of true dielectric particle. On the other hand, according to Hanai\(^{21,22} \) and his co-workers’ investigation,\(^{23} \) phase parameters (the volume fraction, the permittivity, and conductivity of particles and media) can be calculated in principle from relaxation parameters (namely the limiting values of permittivity and conductivity at low and high frequencies, respectively) on the basis of Wagner’s equation\(^{18} \) (for dilute suspension) or Hanai’s equation\(^{21} \) (for concentrated suspensions). The Hanai theory and method have been successfully applied to various heterogeneous systems including the conducting microspheres such as the ion-exchange resin beads.\(^{27} \)

Considering that there are few dielectric investigations of suspensions of the semiconductor/polymer core–shell system up to now, we will make an effort to investigate its dielectric behaviors by employing dielectric relaxation spectroscopy (DRS). As it is well-known that the dielectric spectroscopy of heterogeneous systems is unlike infrared spectra (IR), ultraviolet–visible spectra (UV–vis), Raman spectra (Raman, etc.), it means there is no standard dielectric spectroscopy to which it can be traced, since there is a small amount of data of dielectric measurements on well-characterized systems up to now (because most investigations are focused on PS suspensions); meanwhile, it is difficult to generalize due to the complicated environment around particles, although the study of dielectric properties of disperse systems is an active area of research during recent years.

The aim of this work is to show that the dielectric measurement and dielectric analysis can disclose the dielectric properties of suspensions for well-defined particles composed of two compositions, organic particles (PS) coated with a thin layer of inorganic semiconductor materials (ZnO), and we hope to expand the experimental database or theoretical reference in anticipation of future modeling studies of dielectric relaxation spectroscopy. Therefore, the dielectric measurements of PS/ZnO core–shell microspheres over a frequency range of 40 Hz to 110 MHz is performed. Special emphasis is focused on the dependence of the dielectric parameters on electrolyte concentration and volume fraction of particles. Some of the important results are compared with results of related research works in order to clearly discover the multirelaxation mechanisms and corresponding relaxation behaviors. Moreover, phase parameters of the system which roughly present individual dielectric behaviors of particles have been calculated from dielectric parameters by using the Hanai method, roughly looking at the core–shell sphere as a unitary sphere. Correspondingly, some reasonable explanations are proposed to elucidate the results on the basis of data of dielectric measurements of spherical PS/ZnO suspensions.

2. Experimental Section and Methods

**Particle Suspensions.** The samples investigated in this work were the suspensions of monodisperse spherical PS/ZnO particles with about 0.8–1 μm radii, which were fabricated as described in a previous report.\(^{11} \) The samples were purified with distilled water to remove adsorbing ions on the surface of particles using the dialyzing method until the conductivity of the supernatant was around \( 1 \times 10^{-6} \) S/m.

First, we collected the samples by using the high-velocity centrifugal machine and redispersed them in distilled water at a maximum volume fraction up to 35% approximately (note: the volume fraction in the phase parameters is the value calculated by the Hanai method, here the maximum volume fraction 35% is used as a rough criterion). The determination of the maximum volume fraction of particles is determined as follows: given amounts of PS/ZnO particles are dispersed in a 20 mL measuring cylinder which is loaded with 8 mL os distilled water and sonicated for 30 min to disperse any coarse aggregates. Then, it is approximately defined as

\[
\phi_{\text{Tem}} = \frac{V_p}{V_p + V_m} = \frac{V_p}{V_{\text{total}}} = \frac{V_{\text{total}} - 8}{V_{\text{total}}},
\]

where \( \phi_{\text{Tem}} \) is the volume fraction occupied by the particles in the suspension and \( V_p \) and \( V_m \) are the volumes of particles and medium, separately. Then, the above suspensions of particles with the same volume fraction are dialyzed in 1000 mL KCl electrolyte solution with concentrations of 0.05–0.5 mM, one by one. Finally, the dilute suspensions of particles with different electrolyte concentrations were obtained and named as “Sample 0.05–05 mM” one by one, which is presented in section 3.1. Second, the above concentrated suspension (vol. % \( \approx 35\% \)) determined by the method above was diluted with 0.05 mM KCl electrolyte solution step by step, and then, the suspensions of particles with different volume fractions were obtained, which is presenting in section 3.2.

Prior to measuring, each of PS-ZnO suspensions was sonicated for 15 min to disperse any coarse aggregates that may have formed when the suspensions were left standing for a long time. This was particularly necessary for suspensions with higher particle volume fractions.

**Dielectric Measurement.** Dielectric measurements were carried out in frequency range from 40 Hz to 110 MHz on an HP 4294A with Precision Impedance Analyzer (Agilent Technologies) tested and calibrated in accordance with the procedure recommended by the manufacturer, controlled by a personal computer. The amplitude of the applied alternating field was 500 mV, and the measurement temperature was 18 ± 1 °C. The dielectric measurement cell with concentrically cylindrical platinum electrodes was employed, which has been described and used in previous works.\(^{28,29} \) The solution volume used in the experiment was 2 mL in order to submerge the electrodes. Prior to the transformation, all experimental data were subjected to certain corrections\(^{30} \) for the errors arising from measuring cell. First, the experimental data were corrected by the stray capacitance \( C_r \) and cell constant \( C_g \) of the permittivity cell, which were determined by using several standard liquids, such as pure water, ethanol and acetone. The residual inductance \( L_s \) due to the cell assembly and the terminal leads will make errors, so \( L_s \) of the dielectric cell was determined by use of standard KCl solutions with different concentrations. Then the permittivity and conductivity were calculated from the corrected capacittance and conductance based on expressions 1–4:

\[
C_s = \frac{C_s(1 + \omega^2 L_r C_s) + L_r G_s^2}{(1 + \omega^2 L_r C_s)^2 + (\omega L_r G_s)^2} - C_r \tag{1}
\]

\[
G_s = \frac{G_s}{(1 + \omega^2 L_r C_s)^2 + (\omega L_r G_s)^2} \tag{2}
\]
\[
\varepsilon = \frac{C_1 - C_s}{C_1} \tag{3}
\]

\[
\kappa = \frac{G_0 \varepsilon_0}{C_1} \tag{4}
\]

where \(C_s, C_1, G_0, \varepsilon_0\) are the measured and corrected capacitance and conductance, respectively, \(\omega = (2\pi f)\) is the angular frequency, \(\varepsilon_0\) is the permittivity of vacuum equal to 8.8541 \times 10^{-12} \text{ F m}^{-1}, \) and \(\varepsilon\) and \(\kappa\) are the calculated permittivity and conductivity, respectively.

**Determination of Dielectric Parameters from Dielectric Spectra.** Suspensions of PS/ZnO particles were carried out in the frequency range from 40 Hz to 110 MHz on an HP 4294A with Precision Impedance Analyzer, and then the experimental data (permittivity and conductivity changing with frequency) were obtained. After the confirmation of two dispersions for the system, the Cole–Cole formula eq 5 of the two-dispersion terms is used to fit the experimental data of two-dispersion systems to obtain the dielectric parameters: \(^{21}\)

\[
\varepsilon^* = \varepsilon_h + \frac{\varepsilon_i - \varepsilon_{mid}}{1 + (j\omega \tau_h)^{\beta_i}} + \frac{\varepsilon_{mid} - \varepsilon_h}{1 + (j\omega \beta_h)^{\beta_i}} + \frac{\kappa_i}{j\omega \varepsilon_0} + A\omega^{-m} \tag{5}
\]

where \(\omega\) is the angular frequency and \(\varepsilon_0\) is the permittivity of vacuum. \(\tau_i\) and \(\tau_h\) are the relaxation times of the LFDD and HFD, respectively. \(\beta_i\) and \(\beta_h\) are the parameters indicating the distribution of relaxation time \(\tau_i\) and \(\tau_h\), individually. \(A\) and \(m\) in the electrode polarization term are adjustable parameters. In our case, the real part and conductivity part of eq 5 are fitted to experimental data to obtain the dielectric parameters.

It should be pointed out that the limiting conductivity values of high-frequency \(\kappa_h\) and middle-frequency that \(\kappa_{mid}\) cannot be obtained from the above equation. Therefore, \(\kappa_h\) is estimated from the equation: \(^{23}\)

\[
\kappa_h = (\varepsilon_{mid} - \varepsilon_h)2\pi f_0 \varepsilon_0 + \kappa_{mid} \tag{6}
\]

and \(\kappa_{mid}\) is determined from the plot of conductivity using the single Cole–Cole equation to fit the experimental data based on the obtained dielectric parameters (i.e., \(\varepsilon_m, \varepsilon_h, \beta_h, f_0\)). The best-fitting dielectric parameters, obtained by fitting the experimental data with the Cole–Cole equation (eq 5), are displayed in sections 3.1 and 3.2. And \(\kappa_i\) are determined by using equation \(\kappa = \omega \varepsilon_0 \varepsilon^* + \kappa_j^{32}\) to fit the experimental data of conductivity on the basis of the dielectric parameters (i.e., \(\varepsilon_i, \varepsilon_h, \beta_i, f_0\)) earlier obtained from the curve-fitting of eq 5 to experimental data. All of the values of \(\beta\) are around 0.85–0.95 in our best-fitting results, indicating that the dielectric relaxation is closer to the Debye-type relaxation.

**Determination of Phase Parameters.** Whereas relaxation parameters represent the collective properties of a suspension, phase parameters represent the individual electrical properties of constituent phase. Phase parameters can be calculated in principle from relaxation parameters on the basis of the MW relaxation (this relaxation is of interest here) on the basis of Wagner’s equation \(^{18}\) (for diluted suspension) and Hanai’s equation \(^{21–23}\) (for concentrated suspension). Suspensions under the investigation are composed of PS/ZnO core–shell particles, phase parameters of the system which roughly present the individual dielectric behavior of particles can be calculated from dielectric parameters by using the Hanai method, roughly looking the spherical core–shell particle as a unitary microsphere.

The MW interfacial polarization theory can be expressed as the following equation:

\[
\varepsilon^* = \varepsilon_a^* + \frac{2(1 - \varphi)e_d^*}{2 + \varphi} + (1 - \varphi)e_p^* \tag{7}
\]

where the subscripts \(a\) and \(p\) designate the medium and the particle, respectively. \(\varepsilon^*\) represents the complex permittivity and \(\varphi\) is the volume fraction occupied by the particles.

First, for the dilute suspensions, then Hanai developed a method to calculate the phase parameters from the dielectric parameters on the basis of the MW theory. The phase parameters (\(\kappa_a, \kappa_p, \varphi_p\), and \(\varphi_h\)) are calculated from the dielectric parameters \(\varepsilon_{mid}, \kappa_{mid}, \varepsilon_h, \) and \(\kappa_h\) by the following equations:

\[
H(\kappa_a) = \sqrt{\frac{\kappa_{mid}^a - \kappa_h^a - \kappa_a}{\kappa_a - \kappa_{mid}}} - \frac{\kappa_a}{\varepsilon_{mid} - \varepsilon_h} - \frac{\kappa_h}{\varepsilon_h - \kappa_{mid}} \tag{8}
\]

\[
\varphi = \frac{2\varepsilon_h^2(\kappa_{mid}^a - \kappa_h^a) + (\varepsilon_h - \varepsilon_a)(\varepsilon_{mid}^a - \varepsilon_{mid}^h)\kappa_a^2}{(\varepsilon_h - \varepsilon_h^a)^2 + (\varepsilon_{mid} - \varepsilon_h)(2\varepsilon_h + \varepsilon_h^a)^2} \tag{9}
\]

\[
\varepsilon_p^* = \frac{\varepsilon_a^* + \frac{2\kappa_a^2}{\varepsilon_h^2} - \frac{\kappa_a^2}{\varepsilon_h^2} + \frac{2\kappa_a^2}{\varepsilon_h^2} + \frac{\kappa_a^2}{\varepsilon_h^2} + \frac{\kappa_a^2}{\varepsilon_h^2}}{2\varepsilon_h + \varepsilon_h^a} + \varepsilon_h - \varepsilon_a \tag{10}
\]

\[
\kappa_p = \frac{2\kappa_a^2 + \kappa_a^2 + 2(\kappa_{mid}^a - \kappa_h^a)}{\kappa_{mid}^a - \kappa_h^a} \tag{11}
\]

The numerical values of \(\kappa_a\) in eq 8 can be obtained by computer searching with the observed values of the dielectric parameters.

Second, Hanai \(^{21–23}\) developed a systematic method to calculate the phase parameters for concentrated suspensions since their MW dielectric relaxation can be extensively simulated by

\[
\frac{\varepsilon_d^* - \varepsilon_p^* (\varepsilon_a^* + \varepsilon_p^*)^{1/3}}{\varepsilon_{mid}^* - \varepsilon_h^*} = 1 - \varphi \tag{12}
\]

On the basis of eq 12, the formulas related to the limiting values of low- and high- frequencies are given by

\[
\frac{\varepsilon_h - \varepsilon_p}{\varepsilon_a - \varepsilon_p} = 1 - \phi \tag{13}
\]

\[
\varepsilon_{mid} - \frac{3\kappa_{mid}^a - \kappa_h^a - 1}{\kappa_{mid}^a} = 3\left(\frac{\varepsilon_a - \varepsilon_p^*}{\kappa_a - \kappa_p} + \frac{\kappa_{mid}^a}{\kappa_{mid}^a - \kappa_h^a}\right) - \frac{\varepsilon_a}{\kappa_a} \tag{14}
\]

\[
\kappa_h\left(\frac{3}{\varepsilon_h - \varepsilon_h^a} - \frac{1}{\varepsilon_h}\right) = 3\left(\frac{\kappa_a - \kappa_{mid}^a}{\varepsilon_a - \varepsilon_p^*} + \frac{\kappa_{mid}^a}{\varepsilon_h - \varepsilon_p^*}\right) - \frac{\kappa_a}{\varepsilon_a} \tag{15}
\]

and

\[
\frac{\kappa_{mid}^a - \kappa_h^a}{\kappa_a - \kappa_p} \left(\frac{\kappa_a}{\kappa_{mid}^a}\right)^{1/3} = 1 - \varphi \tag{16}
\]

Then, phase parameters also are approximately estimated from the dielectric parameters which are obtained by fitting the Cole–Cole equation (eq 5) to the experimental data and uniting with the eq 6. \(\varepsilon_a^*\) is considered as a constant at a constant temperature.

To examine the validity of dielectric analysis based on Hanai equations, the theoretical relaxation curves calculated from the obtained phase parameters are compared with the experimental ones. The best frequency dependence of theoretical and experimental permittivity and conductivity for PS/ZnO core–shell particles dispersed in 0.05 mM KCl solution is extracted and shown in Figure 1. The theoretical curves are in good agreement with the experimental ones over the frequency of 10^5–10^8 Hz.
indicating that the present dielectric analysis in our case on the MW polarization is appropriate.

3. Results and Discussion

3.1. Dielectric Relaxation of Suspensions of PS/ZnO Particles Dispersed in Electrolyte Solutions with Different KCl Concentrations. Figure 2 shows three-dimensional (3D) representations of the dependency of KCl concentrations ranging from 0.05 to 0.5 mM on dielectric spectroscopy for suspensions of PS/ZnO core–shell particles. The number of dielectric relaxation determined by the spectrum of permittivity ε′ in Figure 2a corresponds to the number of peak represented by the spectrum of dielectric loss ε″ in Figure 2b. The dielectric loss ε″(ω) is presented by the logarithmic derivative ε″(ω) = −(π/2)(dε/3 ln ω) on the basis of the logarithmic derivative of raw ε″(ω) data (ε″(ω) is the real part of the permittivity of the suspensions for a frequency ω of the applied AC field), which shows an excellent representation of the true imaginary part of the permittivity, ε″(ω).33–35

As shown in Figure 2, the dielectric response is characterized by two distinct characteristic relaxations: low- and high-frequency relaxations which are occurred at kilohertz and megahertz frequencies, respectively. The low-frequency relaxation reported by Schwan,36 and developed by Dukhin,15 is identical with the counterion relaxation which is associated with the setup of the ionic concentration gradient around the particle. The high-frequency relaxation (typically in the megahertz field) is owing to the famous MW effect17,18 which is extended by O’Konski16 by taking into account the surface conductivity without any specification of its physical nature. These propositions of the relaxation mechanism will be confirmed by the analysis of the relaxation mechanism in the following section.

According to the determination of dielectric parameters described in the dielectric spectra of section 2, the Cole–Cole formulas of two dispersion terms with the contribution of electrode polarization (Aω−m) are used to fit the experimental data one by one. The best-fitting results are listed in Table 1.

Determination of the High- and Low-Frequency Relaxation Mechanisms. In the frequency range investigated here, two distinct relaxations are characterized in dielectric spectroscopy of suspensions of PS/ZnO core–shell particles in 0.05–0.5 mM KCl electrolyte solution. Generally, suspensions exhibit two types of dielectric relaxation: one at frequencies on the order of DLa2 (where a is the radius of particle and D is the average diffusion coefficient of ions, respectively) is due to the existence of buildup of charges on the solid/liquid interface when the applied field is employed, and the other at higher frequency of order λ3D (where λ is the Debye length), just as investigated by O’Brien,19 is ascribed to the induced polarization of electrical double layer (EDL) where counterion prevails. In fact, both of them are closely related to EDL since dielectric relaxation of suspensions is sensitive to the ratio of the particle size and its double layer thickness which is varied with either ionic strength. The Debye length or the double layer thickness λ−1 can be expressed as37

$$\lambda^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon_r \kappa T}{2\varepsilon C_m}}$$  \hspace{1cm} (17)

In this expression, e is the elementary charge, κ is the Boltzmann constant, T is the absolute temperature (291 ± 1 K), ε0 is the absolute permittivity of vacuum, εr is the permittivity of the continuous medium (80.5), and Cm is the number concentration of counterions or coions in the suspending medium.

It is well-known that the characteristic relaxation time (τ) is the most effective criterion to determine the dielectric mechanism of different types. Here, for the convenient understanding, we introduce the well-known Einstein relaxation equation, $t = \langle x^2 \rangle/2D$, to our analysis. $\langle x^2 \rangle$ and D are the average displacement and the average diffusion coefficient of ions, respectively. The relaxation time of low-frequency relaxation caused by the counterion polarization corresponds to the time for the counterion to transport from one side of the spherical particle to the other side,37 namely, the transporting distance of counterions is on the order of $2(a + \lambda^{-1})$, that is $\langle x^2 \rangle \approx 2(a + \lambda^{-1})$. The relaxation time of high-frequency relaxation due to the MW polarization corresponds to the time that counterions are shaking back and forth in the electric double layer, and that is $\langle x^2 \rangle \approx \lambda^{-1}$. Therefore, the relaxation time of low- and high-frequency relaxations can be separately estimated by

$$\tau_l = \frac{4(a + \lambda^{-1})^2}{2D}$$  \hspace{1cm} (18a)

$$\tau_h = \frac{\lambda^{-2}}{2D}$$  \hspace{1cm} (18b)

where $\tau_l$ and $\tau_h$ are the low- and high-frequency relaxation time, respectively. D is the ion diffusion coefficient ($D_{Kr} \approx D_{Cr} \approx 2.0 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$), and a is the radius of the particle (approximate 1 μm). According to pH = 5.6, the low- and high-frequency relaxation times can be calculated from eq 18, and their orders are $10^{-4}$ s and $10^{-8}$ s, respectively, either of which is in good agreement with the order of $\tau_l (10^{-4} \text{s})$ and $\tau_h (10^{-8} \text{s})$ listed in Table 1. Accordingly, we propose that the high- and low-frequency dielectric relaxations observed in the system are caused by the MW interfacial polarization17,18 and the counterion polarization,36 respectively.

Moreover, on the basis of O’Brien’s work19 for thin double-layer suspensions and eq 17, the dependency of $\tau_h$ on C can be given by

$$\tau_h = \frac{1}{\lambda^2D} = \left(\frac{2e^2}{\varepsilon_0 \varepsilon_r \kappa T}CD\right)^{-1}$$  \hspace{1cm} (19)

Therefore, the relaxation time of this system is inversely proportional to the concentration of electrolyte, which can be confirmed by the dependency $\tau_h$ on C in Figure 3. This linear dependency surely confirms the conclusion that the high frequency dielectric relaxation results from the MW polarization since the relaxation times decreased (or the relaxation frequen-
cies increased) with the increment of KCl concentration, being characteristic of interface polarization.22,28 For a very thin diffuse layer ($\lambda_a \ll 1$, $\lambda_a \gg 18.82$ in our system shown in Table 3) compared with the particle size $a$, at the kHz range, the counterion atmosphere in the liquid is established slowly by ion motion over a distance equivalent to particle radius $a$. Thus, the characteristic time is equal to $\tau_l = a^2/D$ for this charge rearrangement to reach a steady state. Therefore, we can comprehend the similar phenomena of the linear dependency of the low-frequency relaxation time on electrolyte concentration as shown in Figure 3. Namely, the characteristic times for the two relaxations is $\tau_l/\tau_h = (\lambda a)^2$ which is expatiated by O’Brien.19 Furthermore, the ratio $(\lambda a)^2$ is a constant due to the same electrolyte concentration and the same temperature at the same time since eq $17 \lambda = (2e^2C_\infty f_0\varepsilon_0\kappa T)^{1/2}$; therefore, linear dependency of the low-frequency relaxation time on electrolyte concentration has a similar phenomena.

**Dependences of Some Dielectric Parameters on KCl Electrolyte Concentrations.** Figures 4 and 5 show dependences of the limiting permittivity ($\varepsilon_l$ and $\varepsilon_h$) at low and high frequencies and permittivity increments for low- and high-frequency relaxations ($\Delta\varepsilon_l$ and $\Delta\varepsilon_h$) on the KCl electrolyte concentrations, respectively. It is appropriate here to discuss the two main features of Figures 4 and 5. First, $\varepsilon_l$ and $\Delta\varepsilon_l$ increase monotonously with KCl electrolyte concentrations, which shows a consequence of the effects of increasing ionic strength (increasing $\lambda$ or reducing the double layer thickness) on the low-frequency permittivity. Recall that the physical origin of the high values of the permittivity observed at low frequencies is the existence of a gradient of neutral electrolyte concentration.
around the particle when an applied electric field is employed. As ions take a comparatively long time to transfer from one side of the particle to the other side, the buildup of such neutral electrolyte clouds is a slow process, and its phase lag with the applied electric field gives rise to an increased displacement current. Such increased current is sensed macroscopically as high values of \( \varepsilon_l \). The gradients of electrolyte concentration around the particle, denoting the low-frequency dielectric increments, are larger with the accumulation of more ions on both sides of the particles. Therefore, increasing the ionic strength will bring about a larger concentration polarization, a bigger low-frequency dielectric constant \( \varepsilon_l \) and dielectric increments \( \Delta \varepsilon_l \), which is ascribed to the larger gradient on both sides of particles resulting from the increment of the amount of counterions in the double layer and the decreasing \( \lambda^{-1} \) (just as indicated in eq 17). All in all, the values of \( \lambda a \) (i.e., the ratio between the particle size and its double layer thickness) strongly affects the dielectric relaxation of suspensions, especially the low-frequency relaxation, accordingly, \( \varepsilon_l \) and \( \Delta \varepsilon_l \) show monotonous linear dependence on KCl concentrations. Second, high-frequency \( \Delta \varepsilon_h \) or \( \varepsilon_h \) seems no obvious dependence on the KCl concentrations as shown in Figures 4 and 5. This will be discussed in detail in the following. First, when the frequency is higher than the characteristic relaxation frequency of low-frequency relaxation, counterions in the diffuse layer can no longer displace in phase with the applied ac field, meanwhile, they will not transform from one side of the particle to the other side and reach or accumulate on either boundary but just keep oscillating a distance of the order of the Debye length or double layer thickness \( \lambda^{-1} \). Then the high-frequency relaxation occurs, accompanied with the diminishing of the permittivity due to the decreasing of accumulated charges on either side of particles and the increasing of conductivity due to the additional oscillation of counterions, respectively. According to the concept of the MW interfacial polarization, all high-frequency permittivities have the tendency to be close to each other or even the same value. Therefore, the high-frequency dielectric increments \( \Delta \varepsilon_h \) and dielectric constant \( \varepsilon_h \) seems little dependence with the KCl concentrations.

On the other hand, the limiting conductivities of low- and high-frequency relaxations, \( \kappa_l \) and \( \kappa_h \), both are increasing with the KCl concentrations as shown in Figure 6. This is rational results: when increasing the ion strength, more counterions in the diffuse layer can displace in phase with the external ac field at low frequencies, and at high frequencies more counterions in electrical double layer are oscillating in the scale of double layer thickness \( \lambda^{-1} \). Meanwhile, it is observed that \( \Delta \varepsilon_l \) increased in pace with the increasing of KCl concentrations from 0.05 to 0.5 mM from the entire trend, otherwise, \( \Delta \varepsilon_h \) first increases and then decreases with the increment of KCl concentrations as shown in Figure 7, obviously, one can observe that maximum

### Table 3: Phase Parameters Calculated from Dielectric Parameters by Using Hanai Method for Dilute Suspensions

<table>
<thead>
<tr>
<th>KCl concentration (mM)</th>
<th>( \lambda^{-1} )</th>
<th>( \lambda a )</th>
<th>( \varepsilon_l ) (vol.)</th>
<th>( \kappa_l ) (S/m)</th>
<th>( \varepsilon_h )</th>
<th>( \kappa_h ) (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>42.5</td>
<td>18.82</td>
<td>0.0337</td>
<td>0.0029</td>
<td>42.8</td>
<td>0.1251</td>
</tr>
<tr>
<td>0.15</td>
<td>24.5</td>
<td>32.59</td>
<td>0.0315</td>
<td>0.0047</td>
<td>40.5</td>
<td>0.1389</td>
</tr>
<tr>
<td>0.2</td>
<td>21.3</td>
<td>37.64</td>
<td>0.0312</td>
<td>0.0048</td>
<td>40.2</td>
<td>0.1067</td>
</tr>
<tr>
<td>0.3</td>
<td>17.4</td>
<td>46.09</td>
<td>0.0369</td>
<td>0.0037</td>
<td>45.6</td>
<td>0.1611</td>
</tr>
<tr>
<td>0.4</td>
<td>15.0</td>
<td>53.22</td>
<td>0.0400</td>
<td>0.0067</td>
<td>48.5</td>
<td>0.1905</td>
</tr>
<tr>
<td>0.5</td>
<td>13.4</td>
<td>59.51</td>
<td>0.0389</td>
<td>0.0091</td>
<td>47.2</td>
<td>0.1953</td>
</tr>
</tbody>
</table>

Figure 3. Characteristic relaxation time for suspensions of PS-ZnO particles as a function of KCl concentration. ■ and □ indicate the low- and high-frequency relaxation time, respectively. The lines are the linear fitting results of experimental data.

Figure 4. Dependence of the (■) low- and (□) high-frequency limiting permittivities on the KCl electrolyte concentration, respectively.

Figure 5. Dependence of permittivity increments of the (■) low- and (□) high-frequency relaxations on the KCl electrolyte concentration, respectively.

Figure 6. Dependence of the (■) low- and (□) high-frequency limiting conductivities on the KCl electrolyte concentration, respectively.
value of $\Delta\kappa_h$ appeared at the KCl concentration equal to 0.3 mM. The possible reason for this phenomenon is that, when more ions are diffused in the limited electric double layer, the more hindrance of ions endured in the oscillation will be. At low frequencies counterions take a long time to transfer from one side of the particle to the other side, so it means that counterions have the ability, chance, and time to adjust the hindrance and collision of mutual ions in such slow process under the employment of applied electric field. Otherwise, comparatively to speak, at high frequencies such adjustive ability of ions by themselves is not enough to cope with the mutual hindrance of ions. Therefore, $\Delta\kappa_l$ and $\Delta\kappa_h$ shows different dependences on the KCl concentrations just displayed in Figures 6 and 7.

3.2. Dielectric Relaxation of Suspensions of PS/ZnO Particles with Different Volume Fractions Dispersed in 0.05 mM KCl Electrolyte Solution. There are two mechanisms which are currently used to explain the low-frequency dielectric relaxation (LFDR) of suspensions of dispersed particles in electrolyte solutions, which has been mentioned in introduction. The first, the surface diffusion mechanism (SDM) developed by Schwarz$^{13}$ and then by Vogel,$^{42}$ associates the LFDR with diffusion of bound ions along the particle surface without exchanging with the bulk electrolyte ions under the employment of the applied electric field. The second, the volume diffusion mechanism (VDM) proposed by Dukhin,$^{14}$ related the LFDR to the diffusion of free ions in the diffuse double layer. The method for the investigation of each of two diffusion mechanisms is that the relaxation time of VDM varies with the concentration of particles, and that of the SDM mechanism remains constant.$^{13}$ To some extent, which mechanism dominated in systems depends on properties of the systems, especially the characteristics of dispersed particles. Therefore, for further investigation we carried out the experiments of dependences of the low-and high-frequency relaxations on the volume fractions of particles in the present disperse systems, the results are displayed in Figure 8.

Figure 8 shows three-dimensional (3D) representations of the volume fraction dependence on the dielectric spectroscopy of suspensions of PS/ZnO particles dispersed in the 0.05 KCl electrolyte solution. The number of dielectric relaxation determined by the spectrum of permittivity $\varepsilon'$ and conductivity $\kappa$ in Figure 8, panels a and b, also corresponds to the number of peak represented by the spectrum of dielectric loss $\varepsilon''$ in Figure 8c. It indicates that the dielectric behavior of suspensions of PS/ZnO composite particles is dominated by two typical dielectric relaxations: one is the low-frequency relaxation (typically in kHz) caused by the setup of the ionic concentration gradient around the particle, and the other is

![Figure 7. Dependence of conductivity increments of the (■) low- and (□) high-frequency relaxations on the KCl electrolyte concentration, respectively.](image)

![Figure 8. Three-dimensional representations of volume fraction dependency of the (a) permittivity, (b) conductivity, and (c) dielectric loss spectra for suspensions of PS/ZnO composite particles.](image)
the high-frequency relaxation (typically in the megahertz field) ascribed to the famous MW effect. The relaxation mechanisms about the high- and low-frequency relaxations are in agreement with the statement in section 3.1, but here we do not care about them again. Otherwise, we should point out that, as shown in Figure 8, panels a and b, by arrows, when the volume fraction is higher, the low- and high-frequency relaxation frequencies will get much closer. This tendency will be observed in detail in the following section about the dependency of characteristic relaxation time on the volume fractions and can be confirmed by the prediction obtained by Carrique et al. according to the Cole–Cole plots of the dielectric increments of suspensions of spheres as a function of the volume fraction.

According to the determination of dielectric parameters from dielectric spectra in Figure 8, panels a and b, which is clearly stated in section 2, the results obtained are listed in Table 2.

Table 2 shows the dielectric parameters of suspensions of PS/ZnO core–shell spheres dispersed in aqueous solutions with the volume fractions from 0.1129 to 0.2964. For further investigation, the dependence of relaxation time and dielectric increments on the volume fractions will be discussed in detail in the following paragraphs.

**Dependence of the Characteristic Relaxation Time on the Volume Fraction.** For the purpose of further investigation, plot of the characteristic relaxation time \( \tau_D \) given in Table 2 against the volume fraction \( \phi \) is shown in Figure 9. As observed, it shows that the low-frequency relaxation time \( \tau_l \) decreases with the increase of \( \phi \); otherwise, the high-frequency relaxation time \( \tau_h \) increases monotonically with increasing \( \phi \). The former is in accordance with the prediction of the classical VDM model about the dispersion of concentration polarization employed by Shilov and Borkovskaya, and the latter shows the agreement with the prediction of the MW relaxation at high-frequency regime. The detail about them is discussed in the following paragraphs.

First, for low-frequency relaxation time, the characteristic length \( L_D \) (this value indicates the length over which the radial diffusion takes place) is influenced by the distribution of particles on the basis of the following equation:

\[
\tau_l = \frac{2}{L_D} \quad (20)
\]

Then, a reasonable definition for \( L_D \) in the case of moderately concentrated suspension would be

\[
L_D = a \left( 1 + \frac{1}{((\phi')^{-1/3} - 1)^2} \right)^{1/2} \quad (21)
\]

It should be noted that here the value of \( \phi' \) means \( \phi' = (a/b)^3 \), where \( a \) is the radius of spheric particles and \( b \) is half of the average distance between the centers of two neighboring particles. Therefore, when the volume fraction \( \phi' \) increases and \( L_D \) decreases as the number of particles in the vicinity of a given particle is enhanced, the \( \tau_l \) decreases. On the other hand, SDM is absolutely different from VDM, which associated the LFDR with the diffusion of bound ions along the particle surface caused by the applied field rather than the diffusion of free ions in the diffuse double layer; then it must remain constant for the SDM mechanism. Therefore, the number of particles has little effect on \( \tau_l \) if LEDR is dominated by SDM. It can be seen from Figure 9, the low-frequency relaxation time decreases with the increasing volume fraction of particles. Therefore, the low-frequency relaxation process is dominated by VDM for suspensions of PS/ZnO particles under our investigation. It means that the exchange of counterions in the Stern layer with the free ions in the bulk solution in radial direction is the predominant process in the low frequency (kHz range).

Second, the relaxation time for the MW dispersion at high-frequency regime is as follows:

\[
\tau_{MW} = \frac{\varepsilon_m \tau_0}{\kappa_m} \cdot \frac{1}{2(1 - \phi)Du} + 1 \quad (22)
\]

In this equation, \( \varepsilon_m \) is the permittivity of continuous medium, \( \phi \) is the volume fraction of particles, \( Du \) is the dimensionless Dukhin number that measures the relative importance of surface conductance, \( \kappa' \), compared to the bulk electrolyte conductivity

\[
Du = \frac{\kappa'}{\kappa_m a} \quad (23)
\]

where \( \kappa' \) and \( \kappa_m \) are for the surface conductance and bulk conductivity, respectively. The units are [S] and [S][m]−1, respectively. As it is known that \( \kappa' \) increases with \( \chi \) and is independent of volume fraction, therefore, eq 23 predicts an increment in \( \tau_{MW} \) when the volume fraction increases and \( \chi \) keep constant, which is in agreement with the trend as observed in Figure 9.

**Dependences of Some Dielectric Parameters on the Volume Fraction.** To study the effect of relaxation amplitude on volume fractions of PS/ZnO composite particles, plots of conductivity increments \( \Delta \kappa \) and permittivity increments \( \Delta \varepsilon \) listed in Table 2 against volume fractions of dispersed particles are presented in Figures 10 and 11, individually. Both of them show a noteworthy linear dependency between the relaxation amplitude and volume fractions ranging from 11.29% to 29.64%.

Figures 10 and 11 display \( \Delta \kappa \) and \( \Delta \varepsilon \) linearly increase with volume fractions, the reason of which is the semiconducting characteristics of PS/ZnO particles themselves since the conductivity/permittivity of a suspension is composed of conductivities/permittivities of both particles and continuous medium, moreover, the surface structure of ZnO with hydrophilic nature can adsorb charges on its surfaces in the form of ions. Accordingly, either of them will greatly influence the inner properties of particles, especially improve their electric and dielectric properties when the more PS/ZnO composite particles are added into solution.

For further investigation, the volume fraction dependency of special dielectric increments of suspensions of PS/ZnO particles are shown in Figure 12, where \( \Delta \kappa_l = (\kappa_l - \varepsilon_m)/\phi \) and \( \Delta \kappa_h = (\varepsilon_m - \varepsilon_h)/\phi \) denoting the low- and high-frequency relaxation
amplitude of suspensions of particles per unit volume, respectively. From this figure, it can be observed that both \( \Delta \varepsilon_l \) and \( \Delta \varepsilon_h \) are increasing with the enhancement of \( \phi \), which is not inconsistent with the predictions of theory proposed by Delgado et al.\(^{41}\) meanwhile, it has contradiction with the dielectric analytical results for suspensions of polystyrene and palladium nanoparticle chains.\(^{41,47}\) It is well-known that the investigation of dependency of \( \Delta \varepsilon_l \) and \( \Delta \varepsilon_h \) on volume fractions aims to examine the mutual influences of interparticles on the dielectric behavior of suspensions in an environment where the structure of electric double layer of particles differs substantially from those of an isolated particle. When the volume fraction is increasing, the interparticle distance will shorten and mutual action of interparticle will be obviously strengthened. As the reported studies on the dielectric relaxation,\(^{44,47-50}\) increasing the particle concentrations will reduce the effective charges of particle surface due to the mutual overlap of electrical double layer of particles. Therefore, both \( \Delta \varepsilon_l \) mainly ascribed to the smaller counterion concentration in the diffuse layer and then \( \Delta \varepsilon_h \) due to a relatively smaller ion concentration gradient in the adjoining bulk solution, are decreasing with the increment of \( \phi \), just as concluded from some former works. Otherwise, the results of disperse system under our present investigation are opposite to those of the previous dielectric study of dispersed particles, namely, both \( \Delta \varepsilon_l \) and \( \Delta \varepsilon_h \) are increasing with the increment of \( \phi \) although the effective particle charges are reducing due to the closeness of the counterion cloud.\(^{48}\)

As mentioned above, the change of counterion atmosphere near PS/ZnO particle (namely, the electrical double layer) has obvious characteristic effect on its relaxation amplitude, obviously, our analytical results show that some effect existed in our system on the \( \Delta \varepsilon_l \) and \( \Delta \varepsilon_h \) is much bigger than the effect of counterion atmosphere. We supposed that except for the effect of counterion atmosphere the relaxation amplitude of this system is mainly determined by the structural nature of PS/ZnO core–shell particles themselves since only two main factors, the counterion atmosphere near particles and the self-characteristic of particles, can affect relaxation amplitude. Therefore, if possible we should devote ourselves to calculating phase parameters from dielectric parameters, and then the electric properties of PS/ZnO particles can be gained, which will benefit for our further investigation on dielectric properties of this kind of core–shell systems. The reason for this is that dielectric parameters represent the collective electrical properties of a suspension, and phase parameters represent the individual electrical properties of dispersed phase. Finally, we aim to calculate phase parameters and the results will be displayed in the next section.

### 3.3. Study of the Obtained Phase Parameters

Data presented in Tables 3 and 4 are phase parameters for dilute and concentrated suspensions of PS/ZnO core–shell particles, respectively, which are calculated by the Hanai method as briefly reviewed in the experimental section. \( \varepsilon_p \) and \( \kappa_p \) are the permittivity and conductivity of ZnO/PS core–shell composite particles, separately. \( \kappa_s \) is the conductivity of a continuous medium. \( \varepsilon_s \) is the permittivity of a continuous medium (aqueous solution) considered as a constant value 80.5 at 18 ± 1 °C.

In the results, we should point out that two similarities exist in the comparison of data in Tables 3 and 4. First, the values of \( \varepsilon_p \) are not regularly changed with the electrolyte concentration and volume fraction of PS/ZnO particles, individually. It must be stressed here, this is a rational result since \( \varepsilon_p \) is determined by the nature of particle itself and should not vary with the volume fraction of particles and the environment where the
particles existed. To some extent, the difference of ε_{wp} values displayed in Tables 3 and 4 are considered as the little errors of the curve-fitting and the experiment. Second, the conductivity of dispersed particles ε_{wp} is much bigger than the conductivity of continuous medium ε_{w}. This is also a rational result since the conducting characteristics of PS/ZnO core–shell particles and the charges on their surfaces in the form of ions will greatly influence the inner properties of particles, especially improve their electric properties.

Moreover, an important and unusual result obtained from the values in Tables 3 and 4 is each of the permittivities of PS/ZnO particles dispersed in solution is in the range from 40 to 52. As we know that water molecules can penetrate into ZnO-shell layer due to the effect of hydration of ZnO. Under this condition, the contribution of water on the permittivity of PS/ZnO particles can be eliminated24 according to the expression of

\[ ε_p = f_w ε_w + (1 - f_w) ε_{PS/ZnO} \]  

(24)

where \( f_w \) is the maximal volume fraction of water penetrated into the ZnO-shell layer. Note: the maximum of \( f_w \) is the ratio of volume fraction of ZnO-shell and PS/ZnO microsphere for single particle, which is average value 0.08 according to the radius of PS/ZnO microspheres (0.8–1 um) and the thickness of ZnO layer (25–30 nm). \( ε_w \) (80.5, at 18 ± 1 °C) is permittivity of aqueous solution. \( ε_{PS/ZnO} \), listed in Table 5, panels a and b, for dilute and concentrated suspensions, respectively, is the permittivities of PS/ZnO particles calculated from the eq 24 after eliminating the contribution of water from the permittivity of whole particles on the basis of data in Tables 3 and 4.

According to the investigation reported by Langton51 over the frequency range of 100 kc/s to 10 Mc/s, the maximum value of an acicular ZnO permittivity is 40. Meanwhile, measurements at a frequency of 1 kc/s made by Mujamoto and his coworkers,52 gave a value for the permittivity of ZnO as 11.0 at 15 °C, although no details are given in any of these references of the particle size or shape of the ZnO used. This means permittivity of ZnO particles approximately is ranging from 11 to 40 according to the frequency in the crystalline structure. The permittivity of ZnO existed PS/ZnO microspheres should be less than 40 at least; meanwhile, it is known that the permittivity of polymeric particles (PS) is approximate 2–8. Therefore, according to the MG approximation33–34 or the Hanai eq 12, the permittivity of PS/ZnO composite particle should be much less than 40 or at least in the range of 11–40 by a cursory evaluation. Obviously, the permittivity of PS/ZnO composite particle listed in Table 5, parts a and b, are not very convincing since they exceed the maximum value (40) of an acicular ZnO permittivity. This means that there was something wrong in the calculation of phase parameters. Recall that Hanai et al.21–23 developed a systematic method for calculating phase parameters from dielectric data in a spherical disperse system, which is based on the MW interfacial polarization. Under the present understanding, there are two possibilities that cause discrepancies in the calculation of phase parameters: one is the limiting dielectric parameters of the low-frequency relaxation around 10^{3}–10^{5} Hz and the other is the ones of the frequency relaxation around 10^{6}–10^{9} Hz (here named the “third relaxation”), since the high-frequency relaxation (the MW relaxation) around 10^{6}–10^{9} Hz occurs between the low-frequency and the third relaxation from the point of frequency field. The former has been considered in the calculation of phase parameters in the Hanai method and it is also obviously separated with the MW relaxation in the present investigation; therefore, we can ignore its effect on the MW relaxation. Otherwise, the latter is not taken into account in the calculation of phase parameters, and if it is truly present in the dielectric behavior, it will have an effect on the calculation since the low-frequency limiting permittivity and conductivity of the third relaxation is the high-frequency ones of the MW relaxation.

In order to investigate the system further, lets recall the structure of PS/ZnO particles: PS is the core and ZnO is a thin layer shell of particles which as a typical type of semiconducting particle exhibits strong n-type conductivity with the electrons moving in the conduction band as the charge carriers.55 Therefore, when an alternating electric field is applied to suspensions of PS/ZnO core–shell particles, the motion of charge carriers inside the semiconducting ZnO-shell leads to the development of an internal double layer and a back field that opposes the driving field, which can be confirmed by the prediction of O’Brien on dielectric response of a dilute suspension of semiconducting particles20 and the study of Trukhan on the widely applicable model of a heterogeneous medium, namely, conducting spherical particles in an insulator.56

The analytical process in detail is as follows: the time required for this charge distribution to reach a steady state is on the order of \( a^2/D \), where \( D \) is the charge carrier diffusivity and the value of which is approximately equal to \( 10^{-3} \) m^{2} s^{-1}. For example, the diffusivity of an electron in silicon is \( 3 \times 10^{-3} \) m^{2} s^{-1} and that of a hole is \( 1.4 \times 10^{-3} \) m^{2} s^{-1},72 so the time for internal charge rearrangement in a 1 \( \mu \)m radius silicon particle is \( 10^{-9} \) s,55 meanwhile, the same time is approximately needed for the semiconducting microspheres including just like ZnO. As has been expatiate above, the time for the internal charge rearrangement is much smaller than that of the relaxation time for the double layer polarization since the diffusivity of electrolyte ions is of an order \( 10^{-7}–10^{-9} \) m^{2} s^{-1}. Thus, over the megahertz frequency range where suspension of semiconducting microspheres exhibits the third relaxation caused by the polarization of the internal double layer when the applied field is employed. For the ZnO-shell layer of PS/ZnO composite particles, the distance for charge carrier diffusion is about a half that of the PS/ ZnO spherical perimeter. Then, the time required for the charge carriers rearrange in PS/ZnO composite microspheres is about on the order of \( 10^{-9} \) s or even longer \((t=(\pi a^2)/D)\), which is much closer to that of the MW dielectric relaxation.

Therefore, we suppose that over the megahertz frequency range, where suspension of PS/ZnO particles exhibits the third relaxation caused by the polarization of the internal double layer, which is a result of very high mobility of the charge carriers in the ZnO-shell layer of particles. Moreover, the polarized ramification of the internal double layer formed the third relaxation can work on the contribution of the MW interfacial polarization; therefore, it is most possible that the discrepancy deduced from the calculation of phase parameters is caused by polarization of the internal double layer since the calculation of the Hanai method is based on the MW interfacial polarization.

### Table 5: Permittivities of PS/ZnO Particles after Eliminating the Contribution of Water from It, for the Dilute (a) and Concentrated (b) Suspensions, Respectively

<table>
<thead>
<tr>
<th>KCl (mM)</th>
<th>( ε_p )</th>
<th>( ε_{PS/ZnO} )</th>
<th>( f_w )</th>
<th>( ε_w )</th>
<th>( ε_{PS/ZnO} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>42.8</td>
<td>39.52</td>
<td>0.2964</td>
<td>50.53</td>
<td>47.92</td>
</tr>
<tr>
<td>0.15</td>
<td>40.5</td>
<td>37.02</td>
<td>0.2613</td>
<td>53.01</td>
<td>50.62</td>
</tr>
<tr>
<td>0.2</td>
<td>40.2</td>
<td>36.70</td>
<td>0.2192</td>
<td>51.79</td>
<td>49.29</td>
</tr>
<tr>
<td>0.3</td>
<td>45.6</td>
<td>42.57</td>
<td>0.1824</td>
<td>53.20</td>
<td>50.83</td>
</tr>
<tr>
<td>0.4</td>
<td>48.5</td>
<td>45.72</td>
<td>0.1563</td>
<td>51.79</td>
<td>49.29</td>
</tr>
<tr>
<td>0.5</td>
<td>47.2</td>
<td>44.30</td>
<td>0.1129</td>
<td>52.70</td>
<td>50.28</td>
</tr>
</tbody>
</table>
Especially, we must stress that the so-called polarization of the internal double layer is responsible for the special dependence of \( \partial \varepsilon_l \) and \( \partial \varepsilon_h \) on the volume fraction, which is displayed in the analytical result of Figure 12. All in all, for this complicated nature of particle component; and the results of this paper will provide the experimental data or theoretical reference in future modeling study.

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