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Dielectric relaxation of suspensions of nanoscale particles surrounded by a thick electric double layer

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Dielectric relaxations of suspensions of nanoscale silica particles surrounded by a thick electric double layer are investigated to examine the effect of the concentration of particles. It is found that at low concentrations, the low-frequency dispersion gradually merges with the high-frequency one to become a broad dispersion. The relaxation mechanisms are discussed by using the observed relaxation time. The low-frequency dispersion is caused by the electric double layer polarization while the high-frequency dispersion results from the interfacial polarization. The inner characteristics of the dispersed particles and the dispersing media are obtained from a two-step analytical method developed by the authors [K. He and K. Zhao, Langmuir **21**, 11878 (2005)]. With the results of the analysis, Hill's standard electrokinetic model is employed to interpret the merging of the low- and high-frequency dispersions. The discrepancy between the experimentally observed χa and that derived from the model estimation is preliminarily explained by the overlap of an electric double layer.

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I. INTRODUCTION

The suspensions of nanoscale particles have drawn great attention in recent years due to their giant surface area that gives rise to the unique interfacial[1,2] and dielectric[3–5] properties. Since the dielectric measurement of such suspensions can provide a great deal of information on the interface between the nanoscale particles and the dispersing media, various suspensions have been extensively studied. Examples include the early work on the aqueous suspension of polystyrene microspheres[6–8] and the recent report on the various suspensions of nanoscale particles.[9–14] It has been observed that the suspensions of nanoscale particles usually display two dispersions, the low- and high-frequency dispersions, in the ordinary frequency range for dielectric measurements.[14–16] The low-frequency dielectric dispersion (LFDD) is thought to arise from the polarization of the counterions in the electric double layer (EDL) and the high-frequency dispersion (HFD) from the interfacial polarization.

The interfacial polarization theory, developed first by Maxwell[17] and extended by Wagner[18] (M-W theory), explains well the HFD of the dilute suspensions of particles. Based on the M-W theory, Hanai[19] formulated a rigorous method for dielectric analysis to obtain the interior characteristics of the constituent phases of heterogeneous system (the phase parameter) from the low- and high-frequency dielectric limiting values (the dielectric parameter). This method makes it possible to analyze HFD completely and accurately. Meanwhile, he also took a practical step to numerate the phase parameters of the concentrated suspensions of particles with the theoretical formulae he derived.[20] The Hanai theory and method have been successfully applied to many heterogeneous systems.[11,21] In the M-W theory, however, only the bulk electric properties of each constituent phase are considered and the effect of the distribution of the spatial charges near the interface is neglected. As a result, the application of the M-W theory is limited by the assumption that the thickness of the EDL is much smaller than the particle radius. This assumption, under which the effect of EDL is negligible, is abided by most theoretical[22–25] and experimental investigations.[8,14,26] However, it cannot be applied to the systems such as colloids where the EDL thickness is large compared with the particle sizes, especially when the ion strength is low. To deal with these systems, O'Konski[27] further developed the M-W theory by introducing a correctional term, called surface conductivity, to include the effect of the distribution of electric charges in EDL.

On the other hand, the experimental studies have been conducted on the low-frequency dispersion of the colloidal systems because this dispersion is highly sensitive to the surface properties, such as ζ potential, surface smoothness, dynamic properties, and the Stern layer, of the colloidal particles.[10,13] To interpret the low-frequency dispersion, Schwarz[28] developed a surface diffusion model (SDM) by assuming that under the action of applied electrical field, counterions move only along the particle surface without exchanging with the bulk electrolyte ions. This model fits the observed LFDD of some systems, e.g., the aqueous suspensions of polystyrene particle.[29] A relaxation mechanism of LFDD, the volume diffusion mechanism (VDM), was then proposed by Dukhin.[30] This mechanism is associated with the setup of the ionic concentration gradient around the particle. The difference between Schwarz's and Dukhin's mechanisms is that they used different electrokinetic models of EDL and theoretical hypotheses to describe the behavior of the counterions in and outside of EDL. VDM is apparently closer to the real situation because it is impossible for the counterions inside the EDL to refrain from going into the bulk medium. However, the choice between the two mechanisms depends on the characteristics of the system, especially the properties of the dispersed particles. To some extent, both of the two mechanisms can explain the LFDD of the most practical systems, that is to say, the low-frequency dispersion is a combination of behavior described by SDM and that by VDM. Based on the two mechanisms, various modified models of LFDD have been recently proposed and applied to the systems of multifarious features.

For the dispersions of colloidal particles, HFD, caused by the interfacial polarization, always occurs as the characteristic dispersion, LFDD, arises from the counterion polarization in a wide frequency range. The wide frequency dielectric spectroscopy reflects the integrated properties of the suspensions, and the intrinsic relations between these two dispersions[14–16,31] have received attention from investigators. Simultaneously, the theories combining HFD and LFDD as a whole are also proposed by Grosse[23] and Shilov *et al.*[24] However, all of these works are performed under the assumption of a thin double layer. For the suspensions of particles surrounded by a thick EDL, relevant studies are seldom found.

In addition, the standard electrokinetic offers a different explanation for the dielectric dispersion in the wide frequency range.[32–36] This model derives from the relation between polarizability and dielectric increment, and the analytical results are the typical electrokinetic parameters, e.g. the ζ potential and EDL thickness. Without any restriction on the two parameters, the analytical solutions are hardly obtained. Only the numerical solutions are evaluated after the complex mathematic calculations are performed with the aid of computer programs. Early work was achieved by Delacey and White[32] in the framework of the electrokinetic equations for the dilute suspensions of nonconducting spherical particles in the absence of surface conductivity behind the slipping plane. Mangelsdorf and White[33] dealt with the dielectric dispersions appearing in a relatively low-frequency range, not exceeding 1 MHz, because of the numerical instabilities encountered at high frequencies when solving the full equations. Recently, Hill *et al.*[34–36] employed the finite-difference method they devised and a corresponding computer program to extend the applicability of the standard electrokinetic model to a higher frequency range from 1 kHz to well beyond 1 GHz. They also completed the correlative theoretical deduction of the model systems in many cases, such as the bare colloidal particle suspensions[34] and the suspensions of spherical colloidal particles with neutral polymer coating[35] and charged polyelectrolyte coating.[36]

In the present work, dielectric relaxation of suspensions of nanoscale silica particles surrounded by a thick double layer with different concentration of the particles was investigated in the frequency range 10 kHz to 100 MHz. At the concentration of the particles $>4.5\%$, two obvious dispersions are observed at $\sim 10^5$ and $\sim 10^7$ Hz, respectively. As the concentration decreases, the two dispersions gradually merge into one broad dispersion. An analytical method based on a model of the nanoscale particle surrounded by a thick EDL is applied to obtain the detailed dielectric and structural properties of the constituent phases. With the results of the analysis, the merge of the LFDD with the HFD is interpreted by Hill's standard electrokinetic model.

II. MODEL AND METHOD

Because the colloidal particles studied in the experiment are surrounded by a thick EDL, a different analytical method is required to attain the interior dielectric and surface properties of the dispersed particle and the dispersing media. Here, an analytical method, which is developed by the authors and satisfies this situation, is applied.[37] A word should be added here: the so-called dielectric analysis in this paper is performed on the basis of the appropriate theories and models, and uses the dielectric parameters obtained from the dielectric spectroscopy (namely the limiting values of permittivity and conductivity at low and high frequency) to calculate the phase parameters reflecting the inner properties of constituent phases, such as the volume fraction, and the permittivity and conductivity of particle and media, respectively. For convenience, we briefly review the chief characteristics of this method, first the relevant theories and methods, and then the analytical model and procedures.

A. Relevant theories and methods

The M-W interfacial polarization theory can be expressed by the following equation:

$$\varepsilon^* = \varepsilon_m^* \frac{2(1-\phi)\varepsilon_m^* + (1+2\phi)\varepsilon_p^*}{(2+\phi)\varepsilon_m^* + (1-\phi)\varepsilon_p^*}, \tag{1}$$

where the subscripts m and p designate the medium and the particle, respectively; ε represents the permittivity, κ the conductivity, Φ the volume fraction occupied by the particles. Note that the parameters, ε_p, ε_m, κ_p, κ_m, and Φ, are those of the bulk materials of the respective phases without considering the volume charge distribution at the interfaces. Furthermore, O'Konski proposed that κ_s, the conductivity of the EDL, should be added to the κ_p, and therefore obtained a set of the dielectric parameters closer to reality.[27]

Hanai[19] then developed a method to calculate the phase parameters from the dielectric parameters on the basis of the M-W theory. The phase parameters are related to the dielectric parameters, ε_l, ε_h, κ_l, and κ_h, by the following equations:

$$H(\kappa_m) \equiv \sqrt{\frac{\kappa_l\varepsilon_m - \kappa_m\varepsilon_l}{\kappa_h\varepsilon_m - \kappa_m\varepsilon_h}} - \frac{\kappa_m}{\varepsilon_m}\frac{\varepsilon_l - \varepsilon_h}{\kappa_h - \kappa_l} = 0, \tag{2}$$

$$\phi = \frac{\varepsilon_m\varepsilon_h(\kappa_l - \kappa_m)^2 + (\varepsilon_m - \varepsilon_h)(\varepsilon_m\kappa_l^2 - \varepsilon_l\kappa_m^2)}{(\varepsilon_m\kappa_l - \varepsilon_h\kappa_m)^2 + (\varepsilon_l - \varepsilon_h)(2\varepsilon_m + \varepsilon_h)\kappa_m^2}, \tag{3}$$

$$\varepsilon_p = \varepsilon_m \frac{\phi(2\varepsilon_m + \varepsilon_h) - 2(\varepsilon_m - \varepsilon_h)}{\phi(2\varepsilon_m + \varepsilon_h) + \varepsilon_m - \varepsilon_h}, \tag{4}$$

$$\kappa_p = \kappa_m \frac{\phi(2\kappa_m + \kappa_l) + 2(\kappa_l - \kappa_m)}{\phi(2\kappa_m + \kappa_l) - (\kappa_l - \kappa_m)}. \tag{5}$$

The numerical values of κ_m in Eq. (2) can be obtained by computer searching with the observed values of the ε_l, ε_h, κ_l, and κ_h.

B. Analytical model and procedures

The model of the suspension of the silica particles with a thick EDL is illustrated in Fig. 1. In a continuous media with permttivity ε_m^*, the particle of radius a with a complex permittivity $\varepsilon_{\mathrm{rp}}^*$ (the subscript r indicates real) is surrounded by an EDL of thickness χ^{-1}, in which the counterions are distributed such that the particle EDL as a whole maintains electrically neutral. In the suspension of this work, the par-

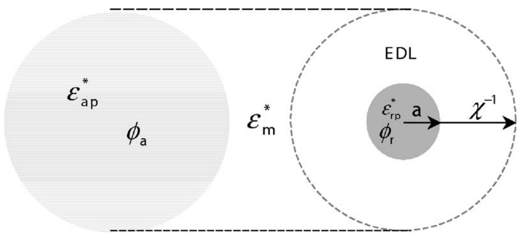

FIG. 1. Schematic drawing of electrical model of the nanoscale silica particle surrounded by a thick electric double layer.

ticle size is small and the ionic strength of the dispersing media is low. It is then safe to assume that the χ^{-1} is larger than the radius of the particle. The real volume fraction occupied by the particle in the whole suspension is Φ_r. The apparent complex permittivity ε^*_{ap} (the subscript a indicates apparent) and apparent volume fraction Φ_a are also defined, including the particle and EDL.

With the variation of particle concentration, two types of suspensions are defined by the number of dispersions: the single-dispersion suspension with low concentration of the particles and the two-dispersion suspension with high concentration of the particles. For the sake of clarity, the flow charts of the analytical procedures of these systems are shown in Fig. 2. The procedures are then described as follows.

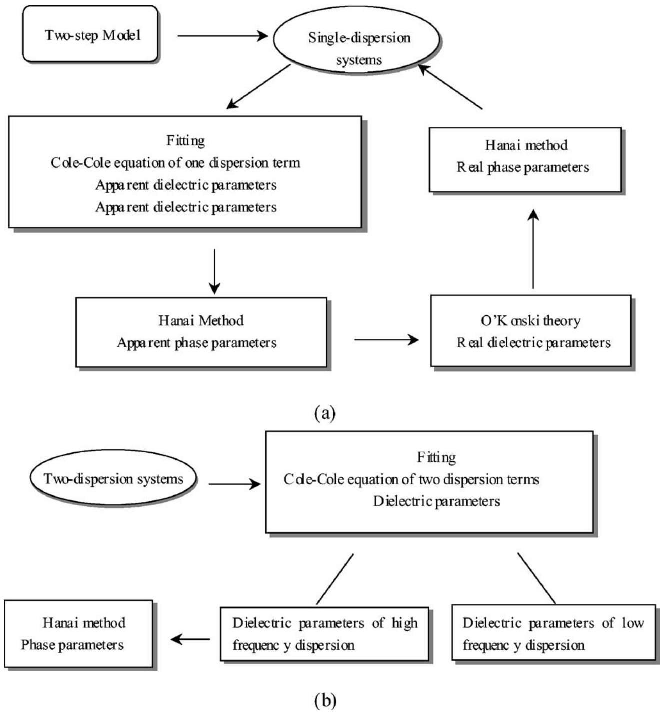

FIG. 2. Flow charts of the dielectric analytical procedures: (a) the single-dispersion system; (b) the two-dispersion system.

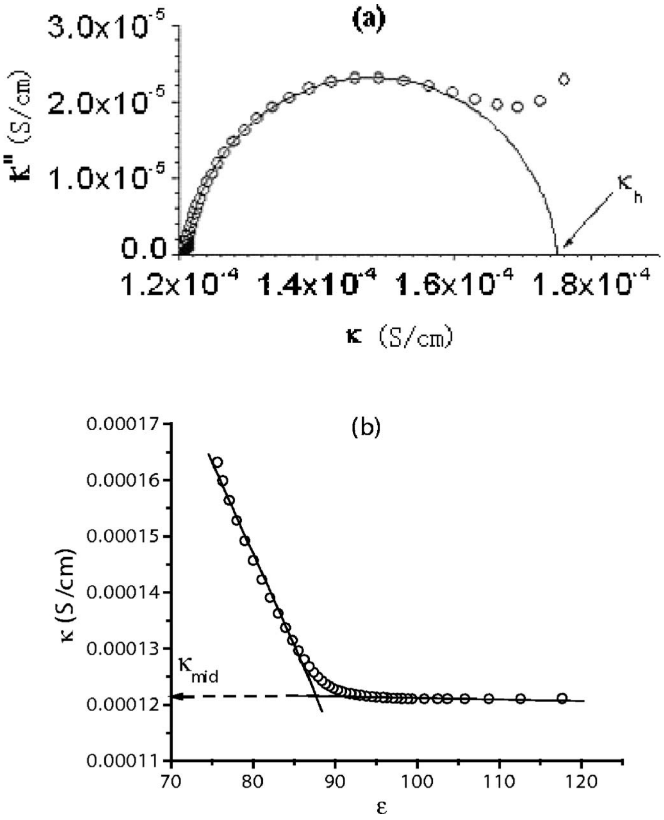

FIG. 3. Atypical result of acquirement of κ_h (a) and κ_{mid} (b): The particle concentration is 10.0%.

1. Analytical procedures of the two-dispersion suspension

The Cole-Cole formula of the two-dispersion terms is used to fit the experimental data of two-dispersion systems to obtain the dielectric parameters:

$$\varepsilon^* = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_{mid}}{1 + (i\omega\tau_l)^{(1-\alpha_l)}} + \frac{\varepsilon_{mid} - \varepsilon_h}{1 + (i\omega\tau_h)^{(1-\alpha_h)}} + \frac{\kappa_l}{i\omega\varepsilon_0}, \qquad (6)$$

where ω is the angular frequency and ε_0 is the permittivity of vacuum. τ_l and τ_h are the relaxation times of the LFDD and HFD, respectively. α_l and α_h are the parameters indicating the dispersion of relaxation time τ_l and τ_h, respectively. It can be seen from that the limiting conductivity values of high-frequency κ_h and middle-frequency that κ_{mid} cannot be obtained from the above equation. Therefore, κ_h is estimated from the complex conductivity plane and κ_{mid} is determined from the plot of conductivity against permittivity. One of the typical results is illustrated in Fig. 3. The experimental points in Fig. 3(b) are characterized by two straight lines and the point of intersection of the two lines gives the value of κ_{mid} with its ordinate.[38–41]

When the concentration of the particles is high and the suspensions display two dispersions, it is reasonable to use the Hanai method to analyze the HFD because its relaxation mechanism is the interfacial polarization. The analytical results reflect the real properties of the constituent phases without the influence of EDL. That is to say, for the two-dispersion systems, the real phase parameters can be obtained by simply using the Hanai method to analyze the HFD [see Fig. 2(b)].

2. Analytical procedures of single-dispersion systems

For the single-dispersion systems, the Cole-Cole formula of one dispersion term is used to fit the experimental data to obtain the dielectric parameters:

$$\varepsilon^* = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_h}{1 + (i\omega\tau)^{1-\alpha}} + \frac{\kappa_l}{i\omega\varepsilon_0}. \tag{7}$$

κ_h can be obtained from the complex conductivity plane. Because the dispersion displayed by these systems is dominated by both of the interfacial and EDL polarization (see Results and Discussion), the fitting results of Eq. (7) include the influence of EDL. The dielectric parameters attained from this equation are the apparent values. According to Fig. 2(a), the phase parameters calculated from the apparent dielectric parameters are spontaneously the apparent phase parameters, which include both of the contributions of EDL and the particle. In order to eliminate the influence of EDL, the apparent phase parameters are in turn introduced into the O'Konski theory to calculate the real dielectric parameters. Then, the results are substituted into the Hanai method again to obtain the real phase parameters. As proved by our previous work,[37] the final results are the real properties of the dispersed particles and the dispersing media.

C. Hill's standard electrokinetic model

Hill's standard elelctrokinetic model is also applied to discuss the interesting dielectric behavior observed in the experiment: the merge of the LFDD with the HFD as the decrease of the concentration of the particles. On the basis of the analytical results, the experimental data are fitted by using this model with the aid of the computer program supplied by R. J. Hill. The electrokinetic parameters are attained such as the EDL thickness and the ζ potential. The model is briefly reviewed here.

Hill *et al.* obtained the dielectric response from the solutions of the governing electrokinetic transport equations.[35] The conductivity and permittivity increments can be expressed in terms of the real and imaginary parts of the polarizability under the oscillatory condition:

$$\Delta\kappa = (\kappa_e - 1)/\phi = 3[\mathrm{Re}(P) + \hat{\omega}\,\mathrm{Im}(P)], \tag{8}$$

$$\Delta\varepsilon = (\varepsilon_e - 1)/\phi = 3[\mathrm{Re}(P) - \hat{\omega}^{-1}\,\mathrm{Im}(P)], \tag{9}$$

where κ_e and ε_e are the effect conductivity and permittivity scaled with the conductivity and permittivity of the dispersing media, κ_m and ε_m. P is the effective polarizability that can be expressed as the following equation:

$$P = D/(\chi a)^3. \tag{10}$$

D is the polarizability scaled with χ^{-3} and can be solved from the Poisson-Boltzman, ion conservation, and momentum conservation equations[35] by using the finite-difference method proposed by Hill *et al.*[42] This model is originally derived from the dispersed particles covered with a polymer shell. However, it also can be applied to the bare particles if the parameters relevant to the characteristics of the shell are neglected.

III. EXPERIMENTAL

A. Particle suspensions

The samples investigated here were kindly supplied by Lanxing Company, China. They were the aqueous suspensions of monodisperse spherical silica particles, 22 nm in particle radius. The samples were purified to eliminate the interferential ions by using the ion exchange adsorption, and then diluted by the distilled water without additional electrolyte added. The pH of these suspensions is about 5.0, so the value of ionic strength is accounted to be 5.0×10^{-6} mol/l. According to the value of pH, χ^{-1} is calculated from the following equation:

$$\chi^{-1} = \left(\frac{8\pi e^2}{\varepsilon_m kT} C\right)^{-1/2}, \tag{11}$$

where e is the elementary charge, k the Boltzman constant, T the absolute temperature, and C the counterion or coion number concentrations far from the particle. The result is $\chi a = 0.81$.

B. Dielectric measurement

The dielectric measurements were carried out using HP 4294A which allowed a continuous frequency measurement from 40 Hz to 110 MHz. The intensity of the applied alternating field was 100 mV and the temperature was maintained constant at (22 °C ± 1 °C). A cell composed of platinum electrodes in a coaxial cylinder, which had been described and used in previous works,[43,44] was used. In order to submerge the electrodes, the measuring volume of the samples was 1 ml. The experimental data were corrected by the cell constant, 0.69 pF, and the stray capacitance, 0.48 pF, which had been determined by use of several standard liquids. The data were also subjected to corrections for errors arising from the residual inductance (0.12 nH) due to the cell assembly.[45]

C. Correction of the electrode polarization

The effect of electrode polarization is a well-known phenomenon due to the accumulation of the spatial charges on the electrode surface, often obscuring the low frequency dielectric dispersion. Considerable efforts have been made to develop ways to eliminate this effect, such as the recent works of Hollingsworth *et al.*[46,47] Their methods remove the influence of electrode polarization effectively. However, a similar result can also be obtained by using an old but valid method.[48,49] This method avoids the design of complex measurement cells. According to this method, the effect of the electrode polarization ε_{EP} is expressed as.[50]

$$\varepsilon_{EP} = Af^{-b}, \tag{12}$$

where A and b are determined from the experimental data of permittivity in low frequency. Using the above equation, the effect of electrode polarization is eliminated from the experimental data and the real dielectric response of the samples is obtained.

IV. RESULTS AND DISCUSSION

A. Dielectric behavior of the suspensions

As a function of frequency, the permittivity and conductivity with different particle concentrations are shown in Fig.

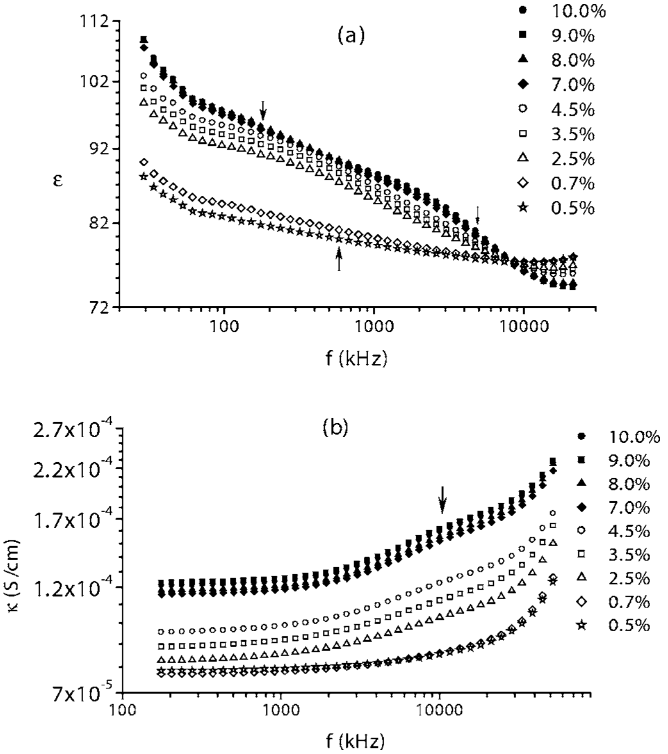

FIG. 4. Dependencies of permittivity (a) and conductivity (b) on frequency for various particle concentrations. The arrows indicate the dispersions.

4. It can be seen from Fig. 4(a), the frequency dependency of permittivity, that when the concentration of the particles is larger than 4.5%, two distinct dispersions are observed and indicated by the arrows in the figure. As the concentration of the particles decreases, the two separated dispersions gradually merge into one. This dispersion covers almost the same frequency region occupied by the two separated dispersions.

The abrupt increase below 50 kHz is thought to arise from the electrode polarization. According to Eq. (12), this effect is corrected, and a typical result is illustrated in Fig. 5. It can be found that the electrode polarization is eliminated. In order to distinguish the two dispersions more clearly, two unattached solid lines calculated from the Cole-Cole formula of one dispersion term [Eq. (7)] are also presented in this figure.

After the effect of electrode polarization is corrected, the Cole-Cole formulae of one and two dispersion terms are used to fit the experimental data, respectively, in order to obtain the dielectric parameters. The results are listed in Table I. It is noticeable that for the single-dispersion systems, these dielectric parameters are the apparent values.

The magnitude of static conductivity (κ_l) presented in Table I increase with the increment of the concentration of the particles. This is because κ_l is composed of two parts of the contributions: the ionic conductivity caused by the migration of ions in the dispersing media, and the electrophoretic conductivity owing to the movement of the charged nanoscale particles.[51] Therefore, when the conductivity of the dispersing media is constant, the increasing number of charged nanoscale particles enhances κ_l.

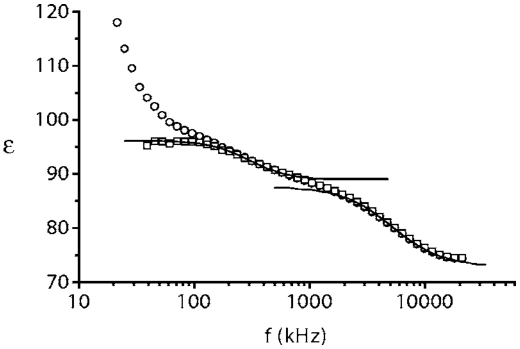

FIG. 5. Correction of the electrode polarization: (○) the experimental data of frequency permittivity dependence, (□) the corrected data of frequency permittivity dependence. Lines are calculated from Eq. (7) to indicate the two separated dispersions clearly. The particle concentration is 10.0%.

B. Analysis of the relaxation mechanism

1. LFDD and HFD of the two-dispersion systems

In the frequency range investigated here, two distinct dispersions are displayed by the suspensions when the concentration of the particles is larger than 4.5%. Although the adscription of the two dispersions' mechanisms has been pointed out in the literature,[6,24] the study of the relaxation mechanism of the suspensions of the small particles surrounded by a thick EDL is seldom reported. Here, the relaxation mechanisms of these special systems will be probed in terms of the relaxation times.

For the ordinary colloidal particle suspensions, Schwarz expressed the order of the relaxation time of LFDD:

$$\tau_l = \frac{a^2}{D} = \frac{a^2}{ukT}, \tag{13}$$

where D is the diffusion coefficient, a the particle radius, u the ionic mobility. If the u value of H^+ in water at 25 °C is $\approx 2.4 \times 10^{12}$ SI units, like Sasaki,[16] the order of τ_l is 10^{-8} s. This value is not in agreement with the experimental results 10^{-7} s (Table I). The difference arises from the hypothesis of the thin double layer in Schwarz's theory. It is our interest to explain why τ_l is one order larger than the theoretical prediction. The interpretation is that the migration of the counterions in EDL is affected by the change of EDL thickness. This change can be demonstrated by the following formula:[52]

$$\tau_l = \frac{a^2}{2D_s}\left(1 + \frac{\lambda}{\varepsilon_0 \varepsilon_m \chi D_s}\right)^{-1} = \frac{a^2}{2D_s + \dfrac{2\lambda}{\varepsilon_0 \varepsilon_m \chi}}, \tag{14}$$

where D_s is the diffusion coefficient of ions in the surface layer and λ is the surface conductivity. This formula differs from that of Schwarz by the factor in the brackets and the substitution of D by D_s. D_s is commonly smaller than D because the counterions inside the Stern layer are more closely bounded around the particle surface. In addition, it is more important that this expression is generalized to the arbitrary χa values, no longer limited to the assumption of thin double layer. Consequently, τ_l will increase if the effect of D_s

TABLE I. Dielectric parameters of the two and single-dispersion systems.

Two-dispersion systems

Particle concentration %	ε_l	ε_{mid}	ε_h	α_l	α_h	τ_l ns	τ_h ns	κ_l μS/cm	κ_{mid} μS/cm	κ_h μS/cm
10.0	96.94	88.58	72.84	0.0557	0.0535	524.1	32.61	121.2	121.4	164.1
9.0	97.16	87.31	73.19	0.1199	0.0186	477.9	32.08	122.8	122.6	161.6
8.0	98.67	86.42	73.22	0.2218	0.0309	488.1	31.58	118.0	116.4	153.4
7.0	97.37	86.09	72.90	0.1895	0.0452	430.3	31.83	115.8	111.7	148.4

Single-dispersion systems

Particle concentration %	ε_{al}	ε_{ah}	α	τ ns	κ_{al} μS/cm	κ_{ah} μS/cm
4.5	96.32	72.08	0.3551	88.20	95.15	170.0
3.5	94.48	73.93	0.3016	104.1	88.22	139.8
2.5	92.06	75.35	0.2364	112.9	82.25	120.5
0.7	85.11	76.23	0.3727	210.2	76.80	99.55
0.5	83.81	76.22	0.4247	278.5	78.10	97.60

on τ_l is larger than the effect of EDL thickness.

As mentioned in the Introduction, the counterion polarization mechanism of LFDD can be classified as SDM and VDM. They cannot be distinguished under the ordinary condition. However, considering the formation and characteristics of LFDD, it is possible to determine which of them prevails in particular conditions. The feature of VDM is that the relaxation time varies with the change of the concentration of the particles because the characteristic length L_D (this value indicates the length over which the radial diffusion takes place) is influenced by the distribution of particles. Then, according to the following equation:[10]

$$\tau_l = \frac{L_D^2}{D}, \tag{15}$$

when the concentration of the particles increases, and L_D decreases as the number of particles in the vicinity of a given particle is enhanced. This results in the decrement of τ_l. If the resistance encountered by the ions when they diffuse is also considered, it is possible to show a relationship contrary to Eq. (15),[13] namely τ_l is proportional to the concentration of the particles. On the other hand, SDM is absolutely different from VDM. The counterions in the Stern layer do not exchange with the free ions in the bulk solution in radial direction but migrate around the particle surface. Therefore, the number of the particles has little effect on τ_l and τ_l is a constant if LFDD is dominated by SDM.

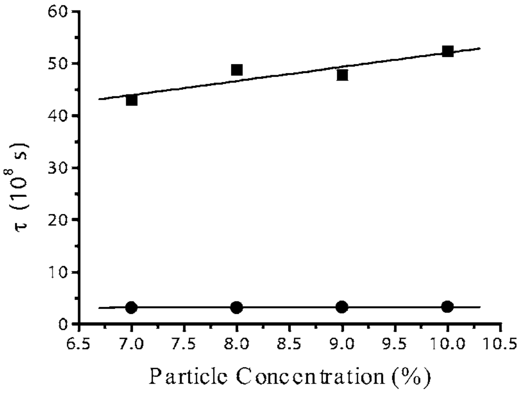

FIG. 6. Dependence of relaxation time of the two-dispersion systems on the particle concentration: (■) indicates the low-frequency dispersion, (●) the high-frequency dispersion.

In order to detect which of the mechanism dominates here, the relaxation times of LFDD and HFD are plotted as a function of the concentration of the particles in Fig. 6. It can be seen from this figure that τ_l increases as the concentration of the particles is increasing but does not keep constant. Therefore, an important conclusion can be drawn: LFDD is predominated by VDM. It must be emphasized here this conclusion is not applicable for all the systems. The relative importance of VDM and SDM must depend on the characteristics of the system.

τ_l in Fig. 6 is proportional to the concentration of the particles, which is contrary to the influence of L_D on the relaxation time. However, when the diffusion occurs, the resistance encountered by the counterions [this resistance is represented by the diffusion coefficient in Eq. (15)] cannot be ignored, especially in the special systems with large EDL thickness. According to $d = 2a(\phi^{-1/3} - 1)$ (the volume fractions Φ are the analytical results),[13] the rough distance between the particles d is estimated. In the scope of the concentration of the particles, d ranges from 35~105 nm, decreasing with the increment of the concentration of the particles. Judging from the minimal interparticle distance, 54 nm (this value is estimated from the value of χa), the double layers of the two neighboring particles overlap with each other when the concentration of the particles >4.5% and thus the movement of ions inside EDL is confined. The

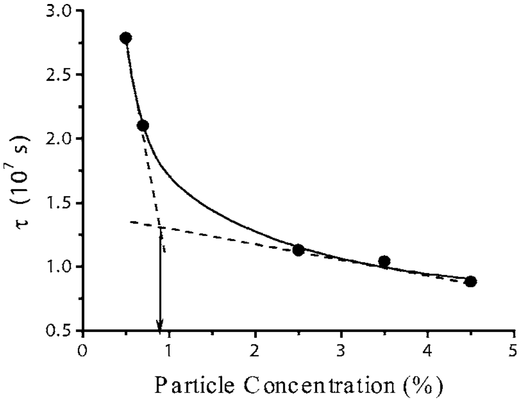

FIG. 7. Dependence of relaxation time of the single-dispersion systems on the particle concentration.

degree of superposition enhances with the increment of the concentration of the particles. Therefore, as the concentration of the particles increases, the two contrary factors, τ_l decreases with the decrement of L_D and τ_l increases with the decrement of D, determine the trend of τ_l together. In this work, the latter, which intimately relates to the thick EDL, is dominant. Accordingly, τ_l increases when the concentration of the particles enhances, just as shown in Fig. 6.

The high frequency dispersion is also observed in the experiment. The relaxation time of this dispersion is approximately 10^{-8} s. According to the M-W theory, the expression of relaxation time τ_h is

$$\tau_h = \frac{2\varepsilon_m + \varepsilon_p + \phi(\varepsilon_m - \varepsilon_p)}{2\kappa_m + \kappa_p + \phi(\kappa_m - \kappa_p)}\varepsilon_0. \tag{16}$$

Using ε_m=79.02, ε_p=3 (the average value of the pure SiO_2), κ_m=95 (μS/cm) (the average value of the following analytical results), $\kappa_p = 10^{-15}$(S/cm) (the value of a pure amorphous SiO_2 like Tepper's work[53]) and $\Phi \approx 0.13$ (an estimated value of the succeeding analysis results), τ_h is calculated to be 75 ns. This value is close to the experimental data (τ_h =32 ns in Table I), indicating that HFD is undoubtedly caused by the M-W interfacial polarization. On the other hand, it can be seen from Eq. (17) that τ_h is relative to Φ. However, within the range of Φ studied here, the magnitude of τ_h calculated from this equation is almost the same, that is to say, τ_h does not change with the concentration of the particles.

2. Dielectric dispersions of the single-dispersion systems

It can be observed in Fig. 4 that only a single dispersion is displayed when the concentration of the particles is lower than 7.0%. The width of this dispersion involves the entire frequency range covered by LFDD and HFD of the two-dispersion systems. As shown by the fitting results given in Table I, the magnitude of the relaxation time of the single-dispersion systems, τ, is exactly between those of LFDD and HFD. Accordingly, this dispersion should not be thought to only arise from the interfacial polarization or counterion polarization but from a combination of these two mechanisms.

Figure 7 is the concentration of the particles dependency of τ. Their relation is no longer similar with that of τ_l which is linear with the concentration of the particles, and also not similar with τ_h (τ_h is unchanged with the concentration of the particles). τ increases with the decrement of the concentration of the particles and abruptly increases at about 0.9%. This trend of τ is neither in agreement with the prediction of the interfacial polarization [Eq. (16)] nor those of SDM [Eqs. (13) and (14), the relaxation time is irrelative to the concentration of the particles] and VDM [Eq. (15)], the relationship of the quadric function). Therefore, according to the above discussion, a satisfying interpretation to the relaxation mechanism of the single dispersion can be given: this dispersion is a combination of behavior described by the interfacial and EDL polarization.

C. Phase parameters

In order to obtain the inner information about the constituent phases and the interface, the dielectric parameters presented in Table I are introduced to the Hanai method to calculate the phase parameters, which represent the inner characteristics of the particle and the media.

Table II presents the phase parameters, including those of the two-dispersion systems and the apparent and real ones of the single-dispersion systems. It is found in the table that the order of the conductivity of the dispersing media, κ_m, is around 10 μS/cm and this is in agreement with that of the distilled water used in the experiment, 65 μS/cm.

The calculated volume fraction Φ in Table II decreases with the decrement of the concentration of the particles and this coincides with the experimental reality. For the single-dispersion systems, the apparent volume fraction Φ_a is obviously larger than the real ones Φ_r, because Φ_a includes both of the contributions of the particles and EDL, whereas Φ_r is the real volume fraction occupied by the particles (see Fig. 1, the model of the particle surrounded by a thick EDL).

The important information about the inner structure of the silica particle can be obtained from the values of the particle permittivity. The values of the calculated ε_p and ε_{rp} are between the permittivity of water (79.02, at 23 °C) and that of the pure silicon dioxide (the average value is about 3). Because the structure of the nanoscale silica particle is porous[54,55] and the water molecules can penetrate into the pores, ε_p and ε_{rp} are between 79.02 and 3. Under this condition, the ε_p can be expressed as:[11]

$$\varepsilon_p = f_w \varepsilon_w + (1 - f_w)\varepsilon_{SiO_2}, \tag{17}$$

where f_w is the volume fraction of water penetrated into the particle, ε_w is the permittivity of water, and ε_{SiO_2} is the permittivity of the pure silicon dioxide. Substituting ε_w=79.02, ε_{SiO_2}=3, and ε_p or ε_{rp} into the above formula, f_w can be obtained as shown in Table III. It is found that f_w ranges from 10% to 55%, indicating that considerable water molecules can penetrate into the silica particle.

D. Merging of the low and high frequency dispersions

After the systematic studies of the relaxation mechanisms and the dielectric analysis, the inner structure and the dielec-

TABLE II. Phase parameters of the two- and single-dispersion systems.

Two-dispersion systems				
Particle concentration %	κ_m μS/cm	Φ	ε_p	κ_p μS/cm
10.0	94.92	0.1578	44.66	427.8
9.0	98.03	0.1466	44.22	424.5
8.0	95.41	0.1284	40.28	420.1
7.0	92.30	0.1224	36.85	411.0

Single-dispersion systems	Apparent phase parameters				Real phase parameters			
Particle concentration %	κ_{am} μS/cm	Φ_a	ε_{ap}	κ_{ap} μS/cm	κ_{rm} μS/cm	Φ_r	ε_{rp}	κ_{rp} μS/cm
4.5	70.77	0.1480	38.88	556.4	75.21	0.07900	12.03	2.294
3.5	67.12	0.1397	46.82	493.0	71.43	0.07074	21.91	2.315
2.5	64.19	0.1334	54.03	411.0	68.59	0.06087	29.74	2.238
0.7	67.75	0.06784	43.64	411.0	70.37	0.03122	13.02	1.815
0.5	70.26	0.05933	39.33	391.7	72.76	0.02585	3.550	1.610

tric characteristics of the constituent phases have been obtained. However, there is a noticeable dielectric behavior that needs to be investigated: LFDD and HFD gradually merge into a broader dispersion with the decrement of the concentration of particles. Therefore, based on an understanding of the relaxation mechanisms and the dielectric properties of the particle and the media, it is necessary to interpret this special behavior.

It can be seen from the change of the relaxation times that τ_l reduces with the dilution of the suspensions, whereas τ_h keeps constant. When the concentration of particles decreases, LFDD shifts towards the high frequency range and HFD does not move along the frequency abscissa. Therefore, they merge into a single dispersion.

Next, the merging of low and high frequency dispersions will be explained in terms of a theoretical model. The model used is Hill's model extended from the well-known standard electrokinetic model. This theoretical model is applied to fit the experimental data to obtain the electrokinetic parameters, such as the double layer thickness and the ζ potential. Other parameters used in the fitting process (the conductivity of media, the permittivity of particle, and the volume fraction) are the analytical results. The fitting curves and results are shown in Fig. 8 and Table IV.

Seen from Fig. 8(a), the fitting curves are in agreement with the experimental data. The real parts of polarizability of the two-dispersion systems display a small dispersion in the high frequency range [indicated by the arrow in Fig. 8(a)] except the large dispersion in low frequency. This small dispersion is incomplete because of the limitation of the fre-

TABLE III. Volume fractions occupied by the water molecules inside a silica particle.

Two-dispersion systems		Single-dispersion systems	
Particle concentration (%)	f_w	Particle concentration (%)	f_w
10.0	0.5479	4.5	0.1188
9.0	0.5421	3.5	0.2487
8.0	0.4903	2.5	0.3517
7.0	0.4452	0.7	0.13180
		0.5	0.007234

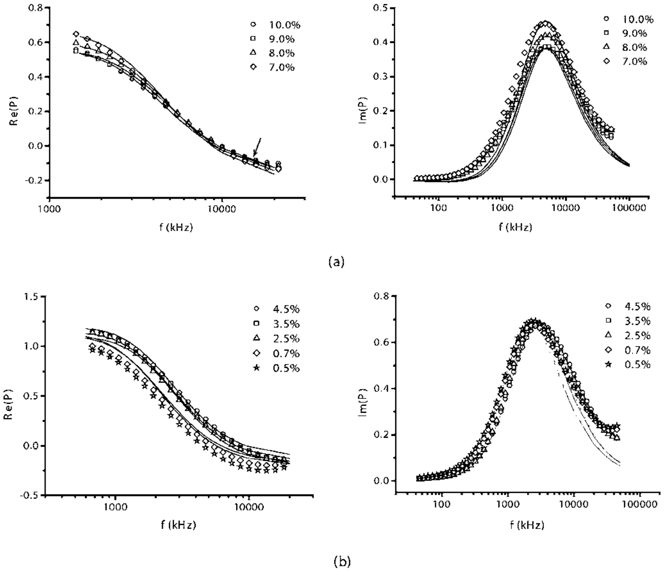

FIG. 8. Real and imaginary parts of polarizability of (a) two-dispersion systems, and (b) single-dispersion systems. Lines are calculated from Hill's standard electrokinetic model.

TABLE IV. Parameters obtained from the fitting results of experimental data, using Hill's model.

Two-dispersion systems				Single-dispersion systems			
Particle concentration %	χa	ζ mV	τ_{D} μs	Particle concentration %	χa	ζ mV	τ_{D} μs
10.0	1.28	−40	0.295	4.5	1.00	−44	0.484
9.0	1.32	−41	0.278	3.5	0.98	−44	0.504
8.0	1.31	−42	0.282	2.5	0.98	−45	0.504
7.0	1.28	−43	0.295	0.7	0.90	−40	0.597
				0.5	0.89	−40	0.611

quency range investigated. However, for the single-dispersion systems, the theoretical model only predicts one dispersion in the whole frequency range and this coincides with the experiment.

According to Hill's model, LFDD and HFD are well separated in frequency only when the radius of the particle is greater than the EDL thickness. Whether the LFDD and HFD appear is intimately related to the value of χa.[34] In Table IV, the magnitude of χa of the single-dispersion systems gradually decreases with the decrement of the concentration of the particles and finally reaches 0.89. This value is close to the observed value 0.81. In this case, LFDD and HFD cannot be observed simultaneously in frequency. For the two-dispersion systems, the value of χa predicted by the Hill's model is larger than 1.0, which means that the low and high frequency dispersions should appear simultaneously. However, this value disagrees with the χa observed. Note that most of the theories, especially the standard electrokinetic model including Hill's model,[32–36] deal with the dilute spherical particle suspensions. Although the highest concentration of particles is only 10.0% in the experiment, it still seems a little higher for the Hill's model. Therefore, when the concentration of particles is larger than 4.5%, Hill's model is not appropriate for these systems. For the systems whose particle concentration is smaller than 7.0%, the values of χa are consistent with the experimental observation.

According to the method used in Hill's work,[35] the characteristic time for diffusion across the double layer τ_D can be evaluated from χa in Table IV, using D_j (the diffusion coefficient of ions in EDL) $\sim 10^{-9}$ m^2 s^{-1}. The order of these values is 10^{-7} s (see Table IV and in agreement with τ_l of the two-dispersion systems. This indicates that LFDD is dominated by the counterion polarization. Another important parameter obtained from Hill's model is the ζ potential ζ. Both for the two-dispersion systems and the single-dispersion systems, its value is similar with that reported in the literature.[56,57]

When the concentration of particles is high, the separation of LFDD and HFD and the difference between the experimental observation and theoretical prediction of the values of χa indicate that there exist unconsidered factors to influence the dielectric behavior of the systems. Taking account of the special properties of our systems, the small particle surrounded by a thick EDL, there is possible to exist interactions between the adjacent particles due to the overlap of EDL in the case of the high concentration of particles. According to the experimentally observed χa, only when the distance between the adjacent particles is larger than 54 nm is there no interaction between them. If the distance is smaller than 54 nm, the overlap of EDL occurs and the circumstance in the vicinity of the particle is much different than that of an isolated particle. This results in the change of the relative properties. It can be seen from the rough estimation of the interparticle distance that this distance increases with the decrement of the concentration of particles. When the concentration of particles is larger than 4.5%, the distance is smaller than 54 nm and the overlap of EDL occurs. Therefore, the overlap of EDL is probably the reason for the separation of LFDD and HFD in the case of the high concentration of particles, though the value of χa observed from the experiment is smaller than 1.0.

V. CONCLUSION

Compared with the ordinary systems studied in most literature, the dielectric behavior of the particle suspensions surrounded by a thick EDL is undoubtedly noticeable. For instance, the relaxation mechanism changes when the concentration of particles changes. This dielectric behavior is intimately related to the properties of the dispersed particle and the dispersing media. In order to obtain the inner information, the combination of the Hanai method and the O'Konski theory is applied to perform the dielectric analysis. It is found from the analytical results that the structure of particles and the characteristics of interface have a remarkable effect on the change of the relaxation mechanisms.

Hill's standard electrokinetic model is applied to investigate the merging of LFDD and HFD when the concentration of particles decreases. The disagreement of χa between the experimental observation and the theoretical prediction is interpreted by the overlap of EDL.

The investigation of the dielectric relaxation of the suspensions of particles surrounded by a thick EDL proves that dielectric spectroscopy is a valid tool to probe the internal characteristics and physico-chemical properties of heterogeneous systems. The results obtained from this work also provide useful information to the correlative scientific field, such as material science.

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