Extension of a Classic Theory of the Low Frequency Dielectric Dispersion of Colloidal Suspensions to the High Frequency Domain

Constantino Grosse

Departamento de Física, Universidad Nacional de Tucumán, Av. Independencia 1800, (4000) San Miguel de Tucumán, Argentina, and Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina

Received: July 8, 2010; Revised Manuscript Received: August 24, 2010

The classic Shilov−Dukhin theory of the low frequency dielectric dispersion of colloidal suspensions in binary electrolyte solutions [Shilov, V. N.; Dukhin, S. S., *Colloid J.* **1970,** *32,* 245.; Dukhin, S. S.; Shilov, V. N. *Dielectric Phenomena and the Double Layer in Disperse Systems and Polyelectrolytes*; Wiley: New York, **1974**] was developed for the frequency range corresponding to the concentration polarization phenomenon: up to a few megahertz. While a few extensions to a broad frequency range including the Maxwell−Wagner−O'Konski dispersion exist, they all consist of modifications of the final results of the theory rather than modifications of its hypothesis, extending their validity to high frequencies. In this work we avoid this artificial process by providing a high frequency extension fully from within the theory.

Introduction

The classic Shilov−Dukhin theory of the low frequency dielectric dispersion (LFDD) of colloidal suspensions in binary electrolyte solutions[1,2] is based on the dc formulation of the concentration polarization.[2−4] It was developed for the frequency range corresponding to this phenomenon so that the obtained analytical expressions are valid for frequencies lower than the onset of the Maxwell−Wagner−O'Konski (MWO) dispersion (typically in the low megahertz range).

Later works by different authors extended the applicability of the theory to higher frequencies including the MWO dispersion, making possible the interpretation of dielectric measurements in a broad frequency range. However, all of these extensions consist of modifications of the final results of the LFDD theory, rather than modifications of the hypothesis used in the original formulation extending their validity to high frequencies.

In the present work we avoid this artificial process by providing a high frequency extension fully from within the theory. To avoid needles repetitions, we use the nomenclature and equations appearing in refs 5 and 6 in which the original formulation was reviewed in full detail and an extension to different counterion and co-ion valences was presented.

Main Results of the Shilov−Dukhin LFDD Theory

The Shilov−Dukhin theory is based on the standard electrokinetic model,[7] so that the suspended particle is represented by an insulating sphere of radius a, with a uniform fixed surface charge density σ_0. The surrounding electrolyte solution is characterized by its viscosity η_e, absolute permittivity ε_e, the unsigned valences of its ions $z^\pm$, their diffusion coefficients $D^\pm$, and their concentrations far from the particle $C^\pm(\infty) = z^\mp N$.

The ion concentrations $C^\pm(\vec{r},t)$, electric potential $\Phi(\vec{r},t)$, fluid velocity $\vec{V}(\vec{r},t)$, and pressure $P(\vec{r},t)$ are determined by the usual set of the Nernst−Planck, continuity, Poisson, Navier−Stokes, and incompressibility equations. These equations are first solved in equilibrium, and then, considering that, a macroscopic ac electric field $Ee^{i\omega t}$ is applied to the system. They are furthermore simplified using the principle of local equilibrium: each sufficiently small volume element of the system is considered to be in a state of equilibrium, even when different volume elements are not in equilibrium with one another. This condition is expressed in terms of a virtual system that is defined by

(i) electroneutrality in its entire volume

$$c^{*\pm} = z^\mp n^*$$

(ii) equilibrium between its volume elements and the corresponding element of the real system

$$\tilde{\mu}^{*\pm} = \ln \frac{C^{*\pm}}{z^\mp N} \pm z^\pm \check{\Phi}^* = \ln \frac{n^*}{N} \pm z^\pm \tilde{\varphi}^*$$

where $c^{*\pm}$ and φ^* are the ion concentrations and the electric potential of the virtual system while $\mu^{*\pm}$ are the electrochemical potentials. In these expressions the asterisk denotes a complex magnitude while the tilde denotes a dimensionless magnitude $\check{\Phi} = \Phi e/(kT)$, $\tilde{\mu}^{*\pm} = \mu^{*\pm}/(kT)$.

The resulting equation set is then linearized, writing all the field-dependent magnitudes as an expansion in successive powers of the applied field strength, for example

$$C^{*\pm} = C_0^\pm + \delta C^{*\pm} + ...$$

where the lower index 0 denotes an equilibrium value while a magnitude preceded by the δ character is linear in the applied field. Combining these expansions with the original equations, dropping all the higher than first-order terms in the applied field, and using the equilibrium expressions finally lead to the following equation system valid outside the equilibrium double layer:

$$\nabla^2 \delta \tilde{n}^* = \kappa^2 \xi^* (\delta \tilde{n}^* + \delta \tilde{\rho}^* z^+ z^- \Delta) \tag{1}$$

Dielectric Dispersion of Colloidal Suspensions

J. Phys. Chem. B, Vol. 114, No. 39, 2010 **12521**

$$\nabla^2 \delta\tilde{\varphi}^* = \kappa^2 \xi^* (\delta\tilde{n}^* \Delta + \delta\tilde{\rho}^* Q) \tag{2}$$

$$\nabla^2 \delta\tilde{\rho}^* = \kappa^2 \delta\tilde{\rho}^* + \kappa^2 \xi^* (\delta\tilde{n}^* \Delta + \delta\tilde{\rho}^* Q) \tag{3}$$

In these equations,

$$\delta\tilde{n}^* = \delta n^* / N$$

$$\delta\tilde{\mu}^{*\pm} = \delta\tilde{n}^* \pm z^{\pm} \delta\tilde{\varphi}^* \tag{4}$$

$$\xi^* = \frac{i\omega}{\kappa^2 D_{\mathrm{ef}}}$$

$$\kappa = \sqrt{\frac{z^+ z^- (z^+ + z^-) e^2 N}{\varepsilon_e kT}} \tag{5}$$

is the reciprocal Debye length,

$$\delta\tilde{\rho}^* = \frac{e}{\kappa^2 \varepsilon_e kT} \delta\rho^* = -(\delta\Phi^* - \delta\tilde{\varphi}^*) \tag{6}$$

is the dimensionless field induced charge density, and

$$\Delta = \frac{D^- - D^+}{z^+ D^+ + z^- D^-} \tag{7}$$

$$D_{\mathrm{ef}} = \frac{(z^+ + z^-) D^+ D^-}{z^+ D^+ + z^- D^-} \tag{8}$$

$$Q = \frac{z^- D^+ + z^+ D^-}{z^+ D^+ + z^- D^-} = 1 + (z^+ - z^-)\Delta \tag{9}$$

The equation set (1)−(3) is solved using the hypothesis of approximate electroneutrality, which states that the electrolyte solution outside the double layer that is electroneutral in equilibrium, remains electroneutral when an ac field is applied:

$$\delta\tilde{\rho}^* = 0 \tag{10}$$

A proof of the validity of this hypothesis is presented in Appendix 1 of ref 6. Equation 10 transforms eqs 1 and 2 into

$$\nabla^2 \delta\tilde{n}^* = \kappa^2 \xi^* \delta\tilde{n}^* \tag{11}$$

$$\nabla^2 \delta\tilde{\varphi}^* = \kappa^2 \xi^* \delta\tilde{n}^* \Delta$$

The appropriate solution of these equations is

$$\delta\tilde{n}^* = K_c^* e^{\xi^{*1/2}\kappa(a-r)} \left(\frac{a}{r}\right)^2 \frac{1 + \sqrt{\xi^*}\kappa r}{1 + \sqrt{\xi^*}\kappa a} \frac{eEa}{kT} \cos\theta \tag{12}$$

$$\delta\tilde{\varphi}^* = \left(\frac{K_d^* a^2}{r^2} - \frac{r}{a}\right) \frac{eEa}{kT} \cos\theta + \delta\tilde{n}^* \Delta \tag{13}$$

where K_c^* and K_d^* are complex frequency dependent integration coefficients. Finally, using eqs 6 and 10

$$\delta\Phi^* = \delta\tilde{\varphi}^* \tag{14}$$

while the field-induced charge density, obtained combining eqs 9, 3, and 11 is

$$\delta\tilde{\rho}^* = \frac{-\xi^* \Delta}{1 + (z^+ - z^-)\xi^* \Delta} \delta\tilde{n}^* \tag{15}$$

The concentration and dipolar coefficients are determined using as boundary condition the integral over r of the continuity equations for the counterion and co-ion flows. The results obtained considering that the double layer is thin as compared to the radius of the particle

$$\kappa a \gg 1 \tag{16}$$

and assuming that the tangential gradient of the electrochemical potential does not change across the double layer are

$$K_c^* = \frac{3 \dfrac{2z^+ z^-}{z^+ + z^-} \dfrac{R^+ - R^-}{2B}}{1 + h^* A/B} \tag{17}$$

$$K_d^* = K_{d\infty} - K_c^* H \tag{18}$$

where $K_{d\infty}$, H, A, and B are real frequency independent coefficients:

$$K_{d\infty} = \lim_{\omega \to \infty} K_d^* = \frac{z^+ D^+ (R^+ - 1) + z^- D^- (R^- - 1)}{z^+ D^+ (R^+ + 2) + z^- D^- (R^- + 2)} \tag{19}$$

$$H = \frac{D_{\mathrm{ef}}(R^+ - R^-)}{z^+ D^+ (R^+ + 2) + z^- D^- (R^- + 2)} \tag{20}$$

$$A = 2 \frac{z^+ D^+ (R^+ + 2) + z^- D^- (R^- + 2)}{z^+ D^+ + z^- D^-}$$

$$B = (R^+ + 2)(R^- + 2) - \frac{z^+ (R^+ + 2)U^- + z^- (R^- + 2)U^+}{z^+ + z^-}$$

$$R^{\pm} = \frac{2z^{\pm}(z^+ + z^-)e^2}{\kappa^2 a \varepsilon_e kT} G_0^{\pm} \pm \frac{3m^{\pm} z^{\pm}}{z^{\mp} \kappa a} I_{\mathrm{eo}}^{\pm} \tag{21}$$

$$U^{\pm} = \frac{3m^{\pm} z^{\pm}}{z^{\mp} \kappa a} (\pm I_{\mathrm{eo}}^{\pm} - z^{\pm} I_{\mathrm{co}}^{\pm}) \tag{22}$$
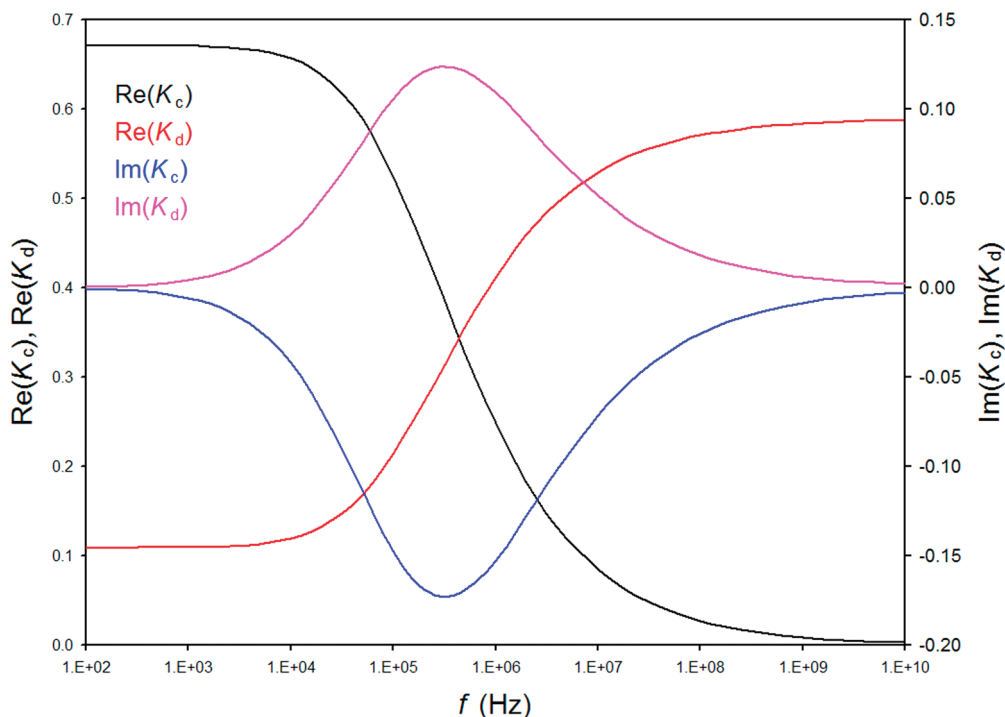
Figure 1. Spectra of the real and imaginary parts of the concentration and dipolar coefficients, eqs 17 and 18, calculated using the parameter values given in Table 1.

$$m^{\pm} = \frac{2\varepsilon_e}{3\eta_e D^{\pm}} \left(\frac{kT}{z^{\pm}e}\right)^2 \qquad (23)$$

while the complex coefficient

$$h^* = \frac{\xi^* \kappa^2 a^2/2}{1 + \sqrt{\xi^*}\kappa a}$$

contains all the frequency dependence. Finally, the analytic expressions for the coefficients $G_0^{\pm}$, $I_{eo}^{\pm}$, and $I_{co}^{\pm}$, related to the nonspecific ion adsorption and the electroosmotic and capillary osmotic fluid flows, respectively, are presented in ref 5. Note that the coefficients $K_{d\infty}$, H, and A have been written in a simpler form than in ref 6, by using the expressions for Δ and D_{ef}, and noting that

$$D^+ U^+ = D^- U^- \qquad (24)$$

The first addend on the right-hand side of eq 18 is proportional to the "fast" part of the dipole coefficient, which is always in phase with the applied field. The second addend is proportional to the "slow" part of this coefficient, which is always in phase with the field-induced concentration change around the particle.

Figure 1 shows the frequency dependence of the real and imaginary parts of the coefficients K_c^* and K_d^*. The system parameters used in this and all the following figures are given in Table 1. As can be seen, the concentration coefficient has the expected behavior in the whole plotted frequency range: a broad single relaxation tending to zero at high frequencies. On the contrary, the frequency behavior of the dipolar coefficient is only acceptable for low frequencies since, at higher frequencies, an MWO relaxation is expected. Another difficulty not readily seen in this figure is that the imaginary part of K_d^* tends

TABLE 1: System Parameter Values Used in All the Figures

particle radius	$a = 100 \times 10^{-9}$ m
particle absolute permittivity	$\varepsilon_i = 2.0\varepsilon_0$
electrolyte solution viscosity	$\eta_e = 8.904 \times 10^{-4}$ poise
electrolyte solution absolute permittivity	$\varepsilon_e = 78.54\varepsilon_0$
ion diffusion coefficients	$D^+ = D^- = 2 \times 10^{-8}$ m²/s
ion concentrations such that	$\kappa a = 30$, $K_e = 0.125$ S/m
dimensionless surface potential	$\tilde{\zeta} = -8$
temperature	$T = 298$ K

too slowly to zero at high frequencies. This becomes evident in Figure 2 where the conductivity and permittivity increments

$$\frac{K - K_e}{\phi} = 3K_e\left[\text{Re}(K_d^*) - \text{Im}(K_d^*)\frac{\omega\varepsilon_e}{K_e}\right] \qquad (25)$$

$$\frac{\varepsilon - \varepsilon_e}{\phi} = 3\varepsilon_e\left[\text{Re}(K_d^*) + \text{Im}(K_d^*)\frac{K_e}{\omega\varepsilon_e}\right] \qquad (26)$$

are shown. In these expressions ϕ is the volume fraction of particles and

$$K_e = \frac{z^+ z^- e^2 N(z^+ D^+ + z^- D^-)}{kT}$$

is the conductivity of the suspending medium. As can be seen, both curves lack the MWO dispersion and, furthermore, the conductivity increment curve diverges instead of tending to a constant limiting high frequency value. Actually, according to rigorous numerical solutions of the full equation set,[8,9] the conductivity increment should reach a maximum and then

Dielectric Dispersion of Colloidal Suspensions

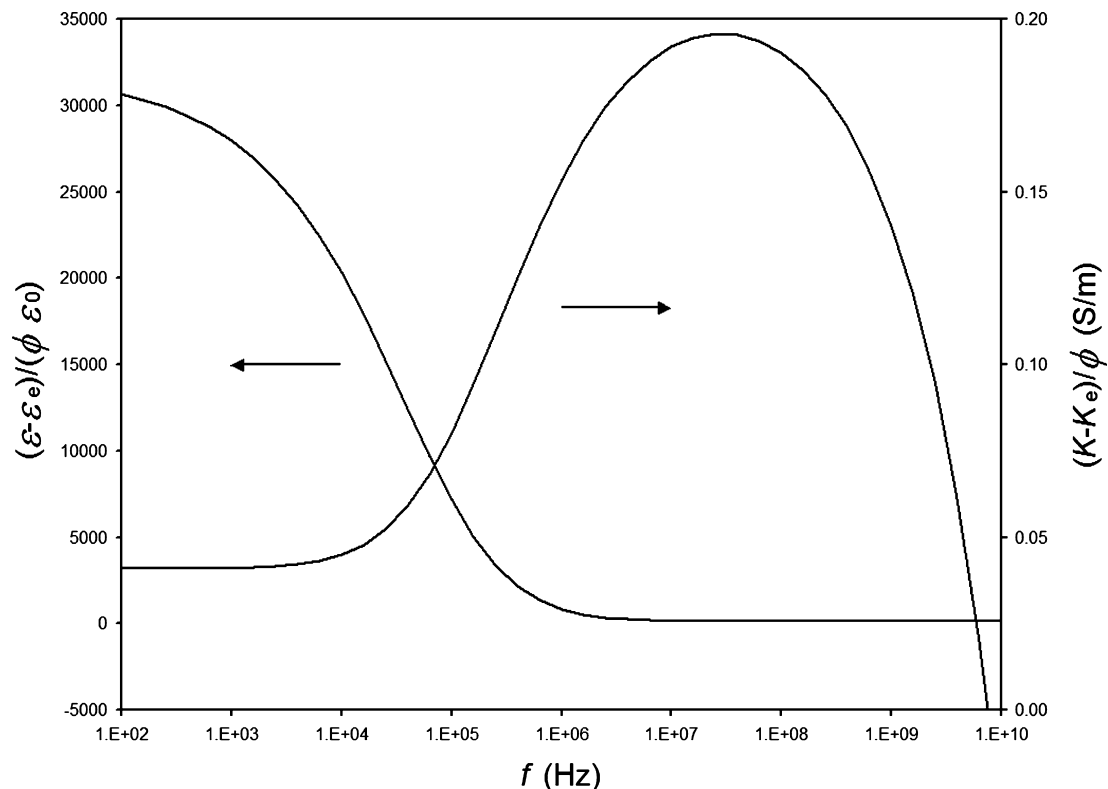*J. Phys. Chem. B, Vol. 114, No. 39, 2010* **12523**

Figure 2. Spectra of the conductivity and permittivity increments, eqs 25 and 26, corresponding to the dipolar coefficient values shown in Figure 1. Remaining parameter values are given in Table 1.

slowly decrease at very high frequencies due to inertial effects, which are not included in the considered theory.

Existing Extensions

There are three existing ways to overcome the above-mentioned difficulties. The first was presented in 1986 by O'Brien,[10] who realized that the high frequency limit $K_{d\infty}$ of the dipolar coefficient, eq 19, coincides with the low frequency limit of the MWO relaxation. So he simply added the corresponding relaxation term to the low frequency expression for the dipolar coefficient transforming transforms eq 18 into:

$$K_d^* = \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} + \frac{K_{d\infty} - \dfrac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e}}{1 + i\omega \dfrac{\varepsilon_i + 2\varepsilon_e}{K_e A/2}} - K_c^* H \qquad (27)$$

where ε_i is the permittivity of the particle. Actually, he used the low frequency expression proposed by Hinch et al.,[11] which is based on the Shilov−Dukhin model rather than their original expression, because it is simpler. Figure 3 shows the frequency dependence of the real part of the dipolar coefficient and of the conductivity increment. As can be seen, O'Brian's extension removes the objection regarding the high frequency behavior of the dipolar coefficient (the MWO relaxation is now present) but does nothing to avoid the high frequency conductivity divergence.

A second extension was proposed in 2001 by Shilov and co-workers.[12] Again, the same relaxation term was added to the high frequency limit of the dipolar coefficient. Furthermore, a factor decreasing exponentially with frequency was added to the low frequency part of the dipolar coefficient:

$$K_d^* = \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} + \frac{K_{d\infty} - \dfrac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e}}{1 + i\omega \dfrac{\varepsilon_i + 2\varepsilon_e}{K_e A/2}} - K_c^* H e^{-\omega \varepsilon_e/K_e}$$

$$(28)$$

As can be seen in Figure 3, this exponential factor successfully solves the objection regarding the high frequency conductivity divergence.

A third extension is based on the usual procedure that consists of calculating the low frequency conductivity and permittivity of the suspension neglecting the addend proportional to $\text{Im}(K_d^*)$ in eq 25 and to $\text{Re}(K_d^*)$ in eq 26. This procedure, justified at low frequencies because the neglected terms are $(\kappa a)^2$ times smaller than the retained ones,[6] eliminates the high frequency divergence of the conductivity. In terms of the dipolar coefficient, it is equivalent to multiplying its low frequency part by the factor K_e/K_e^*,[6] where $K_e^* = K_e + i\omega\varepsilon_e$ is the complex conductivity of the suspending medium. Finally, adding the MWO relaxation to the resulting expression leads to the final result:[13]

$$K_d^* = \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} + \frac{K_{d\infty} - \dfrac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e}}{1 + i\omega \dfrac{\varepsilon_i + 2\varepsilon_e}{K_e A/2}} - \frac{K_c^* H}{1 + i\omega \dfrac{\varepsilon_e}{K_e}}$$

$$(29)$$

As shown in Figure 3, this expression has a frequency dependence that is very similar to that of eq 28, overcoming
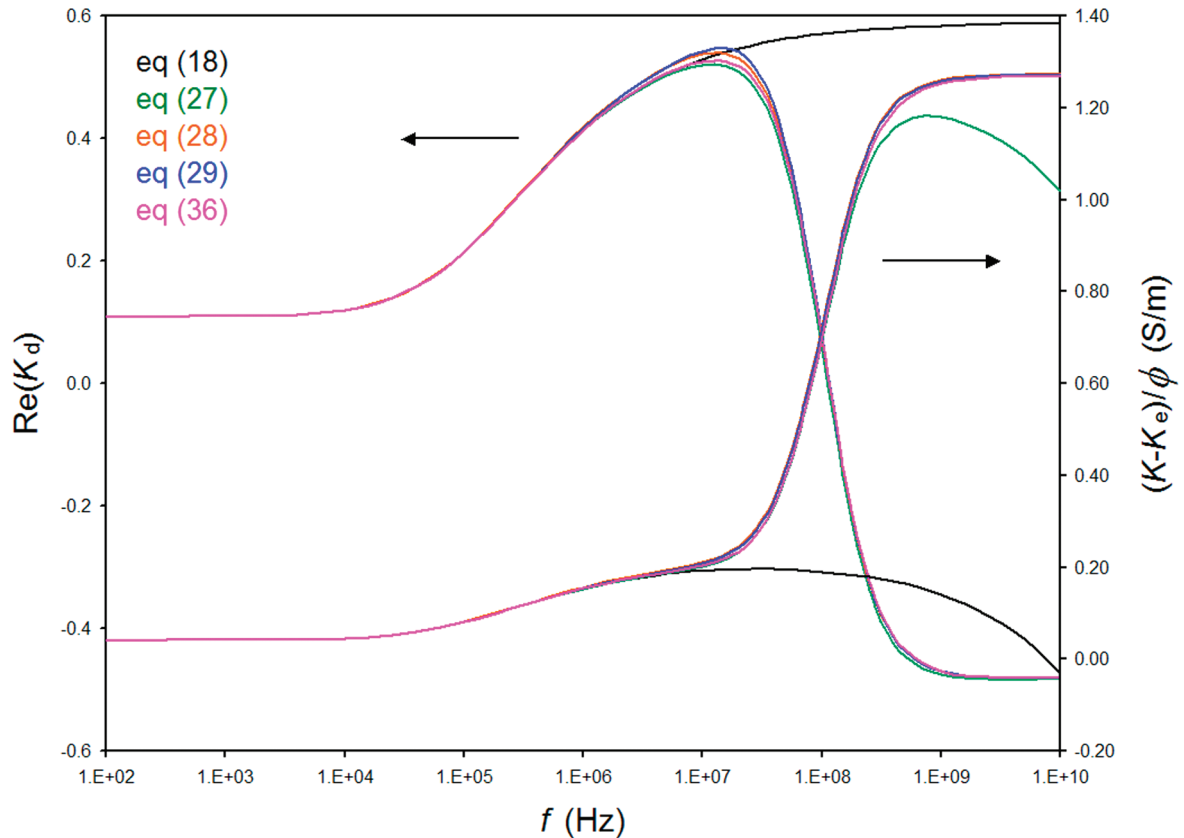
Figure 3. Spectra of the real part of the dipolar coefficients given in eqs 18, 27−29, and 36 and the corresponding conductivity increment spectra. Parameter values are given in Table 1.

both objections regarding the high frequency dispersion and the limiting behavior of the conductivity.

Proposed Extension

To extend the applicability of the theory to high frequencies without introducing artificial modifications to the final low frequency results, it is necessary to reexamine the way in which these results were obtained. The integral over r of the continuity equations for the counterion and co-ion flows, used as boundary conditions to determine the coefficients K_c^* and K_d^*, eq 28 in ref 6 can be written using eqs 4, 5, and 21−23 as

$$-\frac{D^{\pm}}{z^{\pm}}\nabla_r\delta\tilde{\mu}^{*\pm}\Big|_a = \frac{(R^{\pm}-U^{\pm})D^{\pm}}{2z^{\pm}\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\nabla_\theta\delta\tilde{n}^*|_a) \pm$$
$$\frac{D^{\pm}R^{\pm}}{2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\nabla_\theta\delta\tilde{\varphi}^*|_a) -$$
$$\frac{i\omega}{z^+z^-N}\int_a^\infty(\delta C^{*\pm}-z^{\mp}N\delta\tilde{n}^*)\,dr$$

(30)

All the addends in these equations can be expressed in terms of the coefficients K_c^* and K_d^*, except the last. This is why, to obtain the solutions (17)−(18) for these coefficients, the last term in eq 30 is neglected. This is justified noting that this term is proportional to the frequency so that it should be small for the LFDD range. Obviously, this argument no longer holds if the theory is to be extended to high frequencies.

Instead of neglecting the last term in eqs 30, we multiply these equations by $z^{\pm}$ and subtract the second from the first. Using the expressions for the derivatives given in ref 6 together with eqs 7, 8, 20, and 24 leads to

$$K_d^* = K_{d\infty} - K_c^*H - \frac{i\omega}{K_e(A/2)E\cos\theta} \times$$
$$\int_a^\infty(z^+e\delta C^{*+}-z^-e\delta C^{*-})\,dr \quad (31)$$

This expression is identical to the low frequency result, eq 18, except for the last term in which the integral corresponds to the field induced charge density surrounding the particle. In the case $D^+ = D^-$, this integral can be rigorously evaluated using boundary conditions since all the field induced charge is located inside the thin double layer, eq 19 in ref 6. In the general case, however, the procedure is more involved since the charge extends to much greater distances, eqs 12 and 15. In what follows we consider the general $D^+ \neq D^-$ case, keeping in mind that the integral in eq 31 needs only be evaluated at high frequencies since it is multiplied by the frequency so that the last term becomes negligible for $\omega \to 0$.

The field-induced surface charge density of the thin double layer is related to the discontinuity of the radial component of the field-induced displacement:

$$-\varepsilon_e\frac{\partial\delta\Phi^*}{\partial r}\Big|_a + \varepsilon_i\frac{\partial\delta\Phi_i^*}{\partial r}\Big|_a = \int_a^\infty(z^+e\delta C^{*+}-z^-e\delta C^{*-})\,dr -$$
$$\frac{\kappa^2\varepsilon_e kT}{e}\int_a^\infty\delta\tilde{\rho}^*\,dr \quad (32)$$

where $\delta\Phi_i^*$ is the field induced potential inside the particle while the last addend corresponds to the field-induced charge density outside the double layer.

The potential inside the insulating particle, solution of the Laplace equation, can be written as

$$\delta\tilde{\Phi}_i^* = -K_i^* r \frac{eE}{kT} \cos\theta \qquad (33)$$

where the coefficient K_i^* can be determined using as boundary condition the continuity of the field-induced potential across the thin double layer:

$$\delta\tilde{\Phi}_i^*(a) = \delta\tilde{\Phi}^*(a) \qquad (34)$$

In this expression, eqs 13 and 14 for the potential outside the double layer should not be used since, as shown in Appendix I in ref 6, they lead to an expression that is only valid for low frequencies. The general expression valid in the whole frequency range is

$$\delta\tilde{\Phi}^* = \left(\frac{K_d^* a^2}{r^2} - \frac{r}{a}\right)\frac{eEa}{kT}\cos\theta + \frac{\delta\tilde{n}^*\Delta - \delta\tilde{\rho}^*}{1 + \xi^*(Q - z^+z^-\Delta^2)} \qquad (35)$$

Combining eqs 33–35 and neglecting the last addend in eq 35 that rapidly decreases with frequency (and vanishes for $\Delta = 0$ since the field induced charge is then confined to the double layer) lead to

$$K_i^* = 1 - K_d^*$$

This result transforms eq 32 into

$$[K_d^*(\varepsilon_i + 2\varepsilon_e) - \varepsilon_i + \varepsilon_e]E\cos\theta =$$
$$\int_a^\infty (z^+ e\delta C^{*+} - z^- e\delta C^{*-})\, dr - \frac{\kappa^2 \varepsilon_e kT}{e}\int_a^\infty \delta\tilde{\rho}^*\, dr$$

Using eqs 12 and 15, the last integral can be written as

$$\int_a^\infty \delta\tilde{\rho}^*\, dr = \frac{-\xi^* K_c^* \Delta}{1 + (z^+ - z^-)\xi^*\Delta}\frac{eEa}{kT} \times$$
$$\cos\theta \int_a^\infty e^{\xi^{*1/2}\kappa(a-r)}\left(\frac{a}{r}\right)^2 \frac{1 + \sqrt{\xi^*}\kappa r}{1 + \sqrt{\xi^*}\kappa a}\, dr$$

where the integral can be analytically solved

$$\int_a^\infty e^{\xi^{*1/2}\kappa(a-r)}\left(\frac{a}{r}\right)^2 \frac{1 + \sqrt{\xi^*}\kappa r}{1 + \sqrt{\xi^*}\kappa a}\, dr = \frac{a}{1 + \sqrt{\xi^*}\kappa a}$$

The field-induced surface charge density of the double layer so becomes

$$\int_a^\infty (z^+ e\delta C^{*+} - z^- e\delta C^{*-})\, dr = \left\{ K_d^*(\varepsilon_i + 2\varepsilon_e) - \varepsilon_i + \right.$$
$$\left. \varepsilon_e - \frac{\kappa^2 a^2 \varepsilon_e \xi^* K_c^* \Delta}{[1 + (z^+ - z^-)\xi^*\Delta](1 + \sqrt{\xi^*}\kappa a)} \right\}E\cos\theta$$

Neglecting the last addend that becomes negligible at high frequencies (and vanishes for $\Delta = 0$) and using eq 31 leads to the final expression for the dipolar coefficient

$$K_d^* = \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} + \frac{K_{d\infty} - \dfrac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e}}{1 + i\omega\dfrac{\varepsilon_i + 2\varepsilon_e}{K_e A/2}} - \frac{K_c^* H}{1 + i\omega\dfrac{\varepsilon_i + 2\varepsilon_e}{K_e A/2}} \qquad (36)$$

As shown in Figure 3, this result has a behavior that is very similar to the existing extensions, eqs 28 and 29, overcoming both objections regarding the high frequency dispersion and the limiting conductivity value. The high frequency part of eq 36 is actually identical to that of eqs 27−29. As for the low frequency part, the obtained result is very similar to that of eq 29: in both cases the low frequency expression is multiplied by a single time constant relaxation term. The only difference is in the corresponding relaxation time: that of the electrolyte solution, eq 29, or the MWO relaxation, eq 36. It should be noted, however, that the here deduced extension to high frequencies consists of a single modification of both the high and low frequency parts of the dipolar coefficient, rather than two independent modifications of these terms as in eqs 28 and 29.

Conclusion

An extension to the high frequency domain of the classic Shilov−Dukhin LFDD theory is presented. Unlike existing extensions that consist of artificial modifications of the final low frequency results, eq 36 is deduced from within the theory by merely avoiding the approximations that are only justified at low frequencies.

The obtained analytical result is very similar to the existing extensions, eqs 27−29, only differing by the factor that multiplies the low frequency part of the dipolar coefficient. Therefore, the conductivity and permittivity increments deduced using all these expressions combined with eqs 25 and 26 are almost indistinguishable from one another, Figure 4. However, amplifying the part of the spectra that correspond to the MWO dispersion range, Figure 5, shows some differences: the obtained expression has a behavior that is close to that of eq 27. This happens because O'Brien did not introduce any factor multiplying the low frequency part of the original eq 18, while in the presented result this factor becomes different from unity at frequencies that are higher than in eq 29 because the MWO relaxation time is smaller than that of the electrolyte solution.

The differences observed in Figure 5 are not negligible, which suggests that aside from a purely academic interest, the presented extension may be useful for the interpretation of broad frequency dielectric dispersion data of colloidal suspensions. However, two main restrictions of the theory should be kept in mind. First, the thin double layer assumption, eq 16, that limits its applicability to relatively large particles in electrolyte solutions that are not too dilute: $\kappa a \geq 30$ (the actual minimum value further depends on the surface potential[13]). Second, the use of the standard electrokinetic model that does not allow for the existence of a stagnant layer conductivity (an approximate extension of the theory to include this conductivity is given in ref 12). Therefore, in many cases of practical interest, an interpretation based on numerical solutions[8,9] may be required.
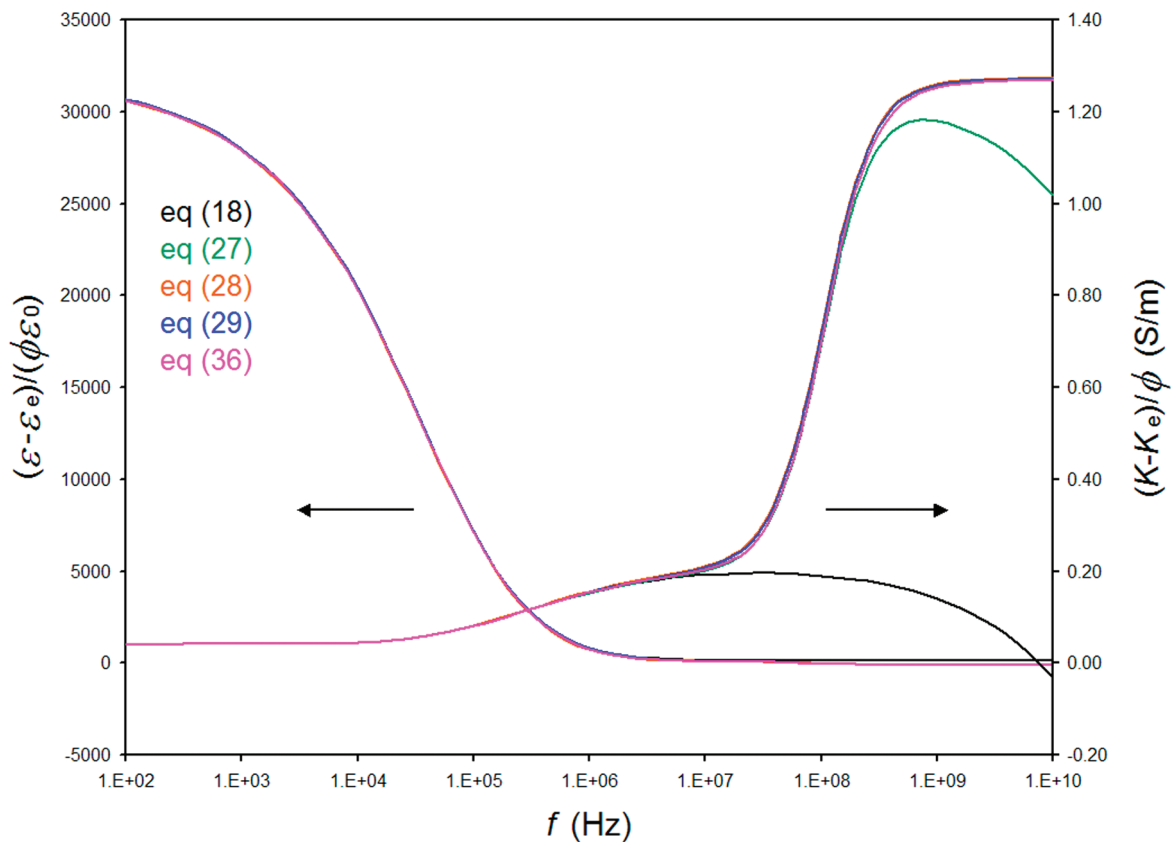
Figure 4. Conductivity and permittivity increment spectra corresponding to the existing, eqs 18 and 27−29, and the proposed, eq 36, dipolar coefficient expressions. System parameter values are given in Table 1.
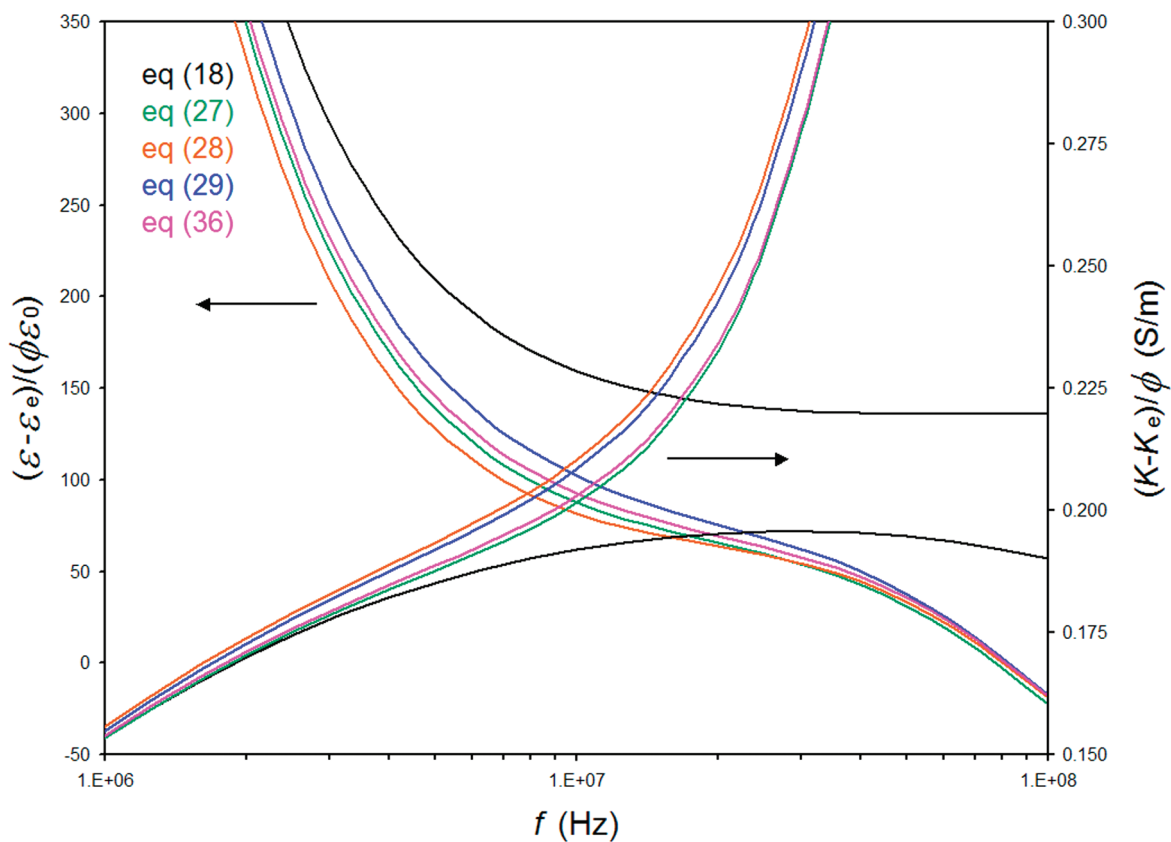
Figure 5. As in Figure 4 but for the frequency range corresponding to the MWO dispersion.

Dielectric Dispersion of Colloidal Suspensions

J. Phys. Chem. B, Vol. 114, No. 39, 2010 **12527**

References and Notes

(1) Shilov, V. N.; Dukhin, S. S. Theory of low-frequency dispersion of dielectric permittivity in suspensions of spherical colloidal particles due to double-layer polarization. *Colloid J.* **1970**, *32*, 245.

(2) Dukhin, S. S.; Shilov, V. N. *Dielectric Phenomena and the Double Layer in Disperse Systems and Polyelectrolytes*; Wiley: New York, 1974.

(3) Dukhin, S. S. In *Research in Surface Forces*; Derjaguin, B. V., Ed.; N.Y.L. Consultants Bureau: New York, 1971; Vol. 3. Translation from: Dukhin, S. S. In *Issledovania v oblasti poverchnostnych sil*; Derjaguin, B. V., Ed.; Nauka: Moscow, 1967.

(4) Dukhin, S. S.; Shilov, V. N. Theory of the static polarization of the diffuse part of the thin double layer of spherical particles. *Kolloidn. Zh.* **1969**, *31*, 706.

(5) Grosse, C. Generalization of a classic thin double layer polarization theory of colloidal suspensions to electrolyte solutions with different ion valences. *J. Phys. Chem. B* **2009**, *113*, 8911.

(6) Grosse, C. Generalization of a classic theory of the low frequency dielectric dispersion of colloidal suspensions to electrolyte solutions with different ion valences. *J. Phys. Chem. B* **2009**, *113*, 11201.

(7) Overbeek, J. Th. G. Theorie der Elektrophorese. Der Relaxation-seffekt. *Kolloid-Beihefte* **1942**, *54*, 287.

(8) Hill, R. J.; Saville, D. A.; Russel, W. B. High-frequency dielectric relaxation of spherical colloidal particles. *Phys. Chem. Chem. Phys.* **2003**, *5*, 911.

(9) Bradshaw-Hajek, B. H.; Miklavcic, S. J.; White, L. R. Frequency-dependent electrical conductivity of concentrated dispersions of spherical colloidal particles. *Langmuir* **2008**, *24*, 4512.

(10) O'Brien, R. W. The high-frequency dielectric dispersion of a colloid. *J. Colloid Interface Sci.* **1986**, *113*, 81.

(11) Hinch, J. E.; Sherwood, J. D.; Chew, W. C.; Sen, P. N. Dielectric response of a dilute suspension of spheres with thin double layers in an asymmetric electrolyte. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 535.

(12) Shilov, V. N.; Delgado, A. V.; González-Caballero, F.; Grosse, C. Thin double layer theory of the wide-frequency range dielectric dispersion of suspensions of non-conducting spherical particles including surface conductivity of the stagnant layer. *Colloids Surf., A* **2001**, *192*, 253.

(13) Grosse, C.; Arroyo, F. J.; Shilov, V.; Delgado, A. V. Numerical results for the dielectric dispersion parameters of colloidal suspensions. *J. Colloid Interface Sci.* **2001**, *242*, 75.