

Dielectric Response of a Dilute Oil-in-Water Emulsion Solution

C.-Y. D. Lu* and J. W. Yu

*Department of Physics, National Central University,
Chung-Li, Taiwan 320, R.O.C.*

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We calculate the dielectric spectra of a dilute solution of charged oil/water emulsion droplets, which have mobile (polarizable) surface charges. The spectrum includes the interfacial polarization (Maxwell-Wagner theory), the double layer polarization (salt relaxation), and the surface charge polarization dispersions. It is found that the dielectric increment of the surface charge relaxation has a large value, and does not always increase with the surface charge density. Assuming a typical magnitude for the surface charge mobility and the ion bulk mobility, we find that the salt relaxation dispersion is likely to overlap with the surface charge relaxation, so that a clean spectrum assignment might be difficult.

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I. Introduction

Dielectric spectroscopy is a quick and non-invasive method for probing the properties of a colloidal suspension. An oil/water emulsion is an oil, water, surfactant mixture in which oil droplets are suspended in the water. The surfactants absorb at the oil/water interface to reduce the surface tension (hence to prolong the life time of this metastable system). A single oil droplet is shown in Fig. 1. Despite the long history of the studies of the dielectric spectrum of emulsions, the early work (see, e.g., a review [1] by Hanai) is restricted to the relative high frequency spectrum where the dispersion is due to the polarization of the water/oil interface. These early data also indicate clearly a rise of the dielectric coefficient at the lowest accessible frequency, around a few kilo Hertz. It was identified as an electrode polarization effect [1], which prevents a further study of the low frequency spectrum. Recently there have been several experimental works on surfactant L_3 phases which overcome this problem and obtain very interesting low frequency spectrum down to a few hundred Hz [2]. It seems that the low frequency spectrum is experimentally more accessible now. This work aims to calculate the dielectric spectrum of the emulsion suspension, where polarization mechanisms slower than the interface polarization are considered. For simplicity, we consider the surface charge which comes from the full dissociation of the ionic groups of the surfactants. The effect of the anneal charge will not be discussed.

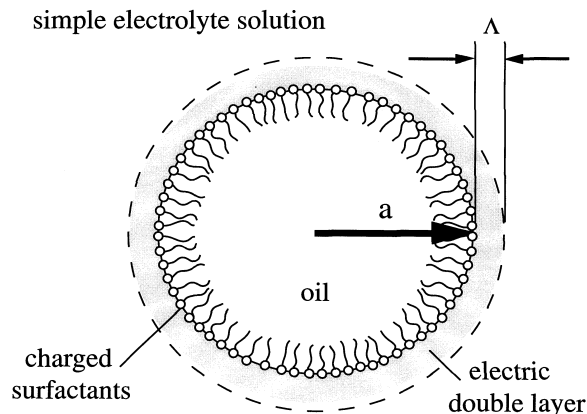


FIG. 1. An oil droplet is suspended in the electrolyte solution. The radius of the droplet is a . The heads of the surfactant molecules all carry charge, of magnitude q per molecule. The electric double layer, which is assumed to be thin, resides between two surfaces $r = a$ and $r = a + \Delta$ (the dashed line).

To get a fuller understanding of the spectrum, one considers together the suspensions of emulsion droplets, latex particles, and bilayer vesicles (e.g. cells). There is an interfacial polarization for both charged and uncharged suspensions, at about GHz for micron size emulsion/latex particles in 0.01M brine. The interfacial polarization is well described by the Maxwell-Wagner theory [1, 3], and its extensions [4-6], where the finite double layer capacitance and the conductance are included.

For micron size charged suspensions, there is a slower relaxation present around one kHz or lower frequencies. The double layer polarization theory explains this as salt relaxation driven by the polarized double layer. The dielectric spectrum has been calculated for latex particles [7-10], and vesicles [6]. For charged emulsion droplets, one expects a similar salt relaxation to appear.

For emulsions and vesicles, the surface charge (the charged amphiphile molecules) can move. The surface charge can either dissolve from the surface into the bulk solution, or redistribute on the surface, and hence be further polarized by the applied field. Therefore one will expect a surface charge relaxation. So far there has been little study of this relaxation, perhaps due to the very low frequencies at which it resides. In fact, the emulsion droplets are particularly suitable as a model system for the effect of a mobile surface charge, because one can tune the droplet size, and the charged surfactant surface mobility (e.g. by using oils with different viscosities).

To establish a model system of mobile surface charge, we consider the no exchange limit where the surfactants are restricted on the surface. Experimentally, the thermodynamic tendency and the kinetic rate of the monolayer to exchange with the bulk solution can be suppressed by using surfactants with long hydrophobic tails. The theory with a dynamic exchange mechanism will involve more delicate assumptions (hence more parameters), and therefore can be better studied if the behaviour of the no exchange limit is well established.

In this paper, by using a single set of equations for all three mechanisms mentioned, we calculate the full dielectric spectrum of a dilute emulsion in the electrolyte solution. We aim at a minimum electrokinetic theory and therefore focus on a simple situation where (1) the double

layer is thin (high electrolyte concentration) compared to the radius of the oil droplets; (2) only the z : z electrolyte is considered; (3) the counterion and the coion have the same mobility μ ; (4) the surfactants are confined on the oil/water interface; (5) the charge surfactants are fully dissociated. Below in section II, the governing equations are presented, which combined the standard thin double layer polarization theory and the Schwarz theory [11]. In section III, we present and discuss the result for the less cumbersome high surface charge regime. A short summary concludes the paper.

II. Governing equations

II-1. Dielectric response

We first recall an expression for the dielectric response by De Lacey and White [9]. Imposing an oscillating electric field $E \exp i\omega t$ on a colloidal dispersion, the proportional (complex) constant between the average current response and the average electric field define the frequency dependent effective conductivity $K_{eff}(\omega)$ and relative dielectric response $\epsilon_{eff}(\omega)$ as:

$$\langle \mathbf{j} \rangle = (K_{eff} + i\omega \epsilon_{eff} \epsilon_0) \langle \mathbf{E} \rangle \quad (1)$$

where \mathbf{j} is the local current, which includes the conduction and the induction contributions. ϵ_0 is the vacuum permittivity. Angle brackets represents the space average, which also includes the space occupied by the double layers and the suspension. Following De Lacey and White [9], for the dilute suspensions, one can use the current expression $\mathbf{j} = (K + i\omega \epsilon_b \epsilon_0) \mathbf{E}$ in the bulk, and the condition $\nabla \cdot \mathbf{j} = 0$ to establish

$$\langle \mathbf{j} \rangle = (K + i\omega \epsilon_b \epsilon_0) \langle \mathbf{E} \rangle + 3AP \langle \mathbf{E} \rangle; \quad (2)$$

where $K = 2q^2 \mu C_0$ is the bulk conductivity, q is the counterion charge, C_0 is the bulk electrolyte concentration, and ϵ_b is the relative dielectric constant of the solvent. The property of the emulsions enters via their volume fraction ϕ and the dipole strength P . The latter is defined by the asymptotic electric potential of one emulsion droplet as $\tilde{A} = \int E \cdot \mathbf{r} (1 + Pa^3/r^3)$ where a is the radius of the droplet and r is the radial coordinate. In general $P = P^0(\omega) + iP^{\infty}(\omega)$ is a complex valued function of ω , which describes the dielectric dispersion. Based on Eq. (2), a theory which calculates the dipole strength P of a emulsion droplet gives the dielectric response of a dilute emulsion solution.

II-2. The bulk solution

In the standard electrokinetic theory, the description of the system involves the electric potential ψ , two concentration fields for the counterion C_+ and the coions C_i , and the flow field \mathbf{v} . The potential obeys the Poisson equation

$$\nabla^2 \psi = -q(C_+ - C_i) / \epsilon_b \epsilon_0; \quad (3)$$

The ion concentrations obey the Smoluchowski equation

$$\partial_t C_s = \nabla \cdot (\mu \nabla C_s - q C_s \nabla \psi + C_s \mathbf{v}); \quad (4)$$

The flow field is incompressible, $\nabla \cdot \mathbf{v} = 0$, and satisfies the Navier-Stoke equation

$$\rho_m (\partial_t + \mathbf{v} \cdot \nabla) \mathbf{v} = -\nabla p - q(C_+ - C_i) \nabla \psi + \eta \nabla^2 \mathbf{v}; \quad (5)$$

where ρ_m is the mass density, p is the pressure, μ_i is the ion mobility, and T is the temperature in energy units.

Instead of C_+ and C_i , one can use the salt concentration perturbation $\pm C = (C_+ + C_i) - 2C_0$ and the charge density $\frac{1}{2} = q(C_+ - C_i)$ to uncouple Eq. (4) as in [12], so that the salt concentration perturbation in the bulk obeys the diffusion equation

$$\frac{\partial}{\partial t} \pm C = D r^{-2} \pm C; \quad (6)$$

where $D = T^{-1}$ is the diffusivity.

In the equilibrium bulk solution, the charge density is zero and the unperturbed electric potential is $\bar{A} = a_0$ (which is just a constant). In the dynamic situation, the charge density and the potential perturbation $\bar{A} = a_0 + \tilde{A}$ now obey [12]

$$\begin{aligned} r^{-2} \tilde{A} &= \frac{1}{2} \tilde{\rho} = \frac{1}{2} \tilde{\rho}_0; \\ \frac{\partial}{\partial t} \tilde{\rho} &= D (r^{-2} \tilde{\rho} - \tilde{\rho}^2); \end{aligned}$$

where the Poisson equation was used in deriving the latter. The Debye length λ_D^{-1} is defined by $\lambda_D^{-2} = 2q^2 C_0 = 2q^2 \rho_0 T$. From the latter equation, any charge excitation can persist at most a few Debye lengths into the bulk, therefore one can set $\tilde{\rho} = 0$ in the bulk. The potential perturbation in the bulk in fact obeys the simpler Laplace equation

$$r^{-2} \tilde{A} = 0 \quad (7)$$

exterior to the double layers. Equation (7) is also valid inside the emulsion droplets. The velocity field outside the double layer obeys the neutral Navier-Stokes equation, which does not contribute any current and will not be needed below. The flow field inside the double layer can be calculated [8] to give the convective current inside the double layer (as discussed below Eq. (15)).

For a spherical emulsion droplet perturbed by an applied electric field, we retain only the solutions of Eqs. (6), (7) with the right symmetry. Outside the double layer this gives $\tilde{A} = \frac{1}{2} E \epsilon r (1 + P a^3 r^{-3})$. Inside the emulsion we have $\tilde{A} = \frac{1}{2} E \epsilon r^{\tilde{P}}$. The concentration perturbation is $\pm C = B \cos \mu \exp(\mu r) \exp(-\mu r)$ with $\mu = \lambda_D^{-1} = D^{-1/2}$. The parameters P , \tilde{P} and B are to be determined later by the boundary conditions.

II-3. The boundary conditions

The diffusion and the Laplace equations govern the salt concentration perturbation and the potential perturbation outside the double layers. Their boundary conditions, which relate quantities adjacent, but exterior to the double layers, can be found from the analysis of ion conservations within the double layers [5, 7, 10]. Below we use the equivalent conditions of the surface excess ionic concentration and the surface excess charge conservation to provide the boundary conditions. This choice of the variables makes the connection with the Maxwell-Wagner theory clearer.

II-3-1. Surface excess

Define the surface excess ionic concentration $\tilde{\rho}_s$ and surface excess charge $\tilde{\rho}_s$ by

$$\tilde{\rho}_s = \int_0^{\infty} (C_+ + C_i - 2C_0) dz = 8 \frac{C_0 + \pm C_a}{\lambda_D} \sinh^2 \frac{q^3}{4T}; \quad (8)$$

$$\int_0^{\infty} q(C_+ - C_-) dz = \frac{4q(C_0 + \pm C_a)}{2T} \sinh \frac{q^3}{2T}; \quad (9)$$

where $\pm C_a$ is the salt concentration perturbation at the edge of the double layer $r = \hat{a} = a + \infty$. Note that the surface excess as defined is not sensitive to the exact value of ∞ as long as it is a few times the Debye length. (The convenient limit $\infty \rightarrow 1$ is taken above to reduce a free parameter. For the far field, which varies at a much larger length scale, the different limit $\infty \rightarrow 0$ will be taken there as a good approximation.) Express the perturbations ϕ and ψ (of ϕ and ψ respectively) in terms of the salt perturbation $\pm C_a$ and the ϕ potential. We have

$$\psi = \int (C_{11}\phi^3 + C_{12}\pm C_a); \quad (10)$$

$$\phi = \int (C_{21}\phi^3 + C_{22}\pm C_a); \quad (11)$$

where we define the scaled concentration perturbation $\pm C = T \pm C_a / qC_0$ and similarly $\pm C_a = T \pm C_a / qC_0$. Note that in deriving Eqs. (10), (11), the Debye length is also perturbed by the perturbation $\pm C_a$. The capacitances are $C_{11} = \frac{2}{b} \frac{2}{0} + C_{22}$, $C_{12} = C_{21} = q\int = 2T$, $C_{22} = q^2 \int = 2T$ as calculated from Eqs. (8), (9). The perturbation of the ϕ potential is simply the difference between the potentials

$$\phi^3 = \tilde{A}_a - \tilde{A}_a; \quad (12)$$

where \tilde{A}_a and \tilde{A}_a are the potential perturbations at $r = a$ and $r = \hat{a} = a + \infty$ respectively.

II-3-2. Surface excess conservation

The conservation law of the excess ion density can be obtained by calculating the normal and the tangential flux contributions of a small piece of the double layer. Using the same method as Fixman [8], we obtain

$$\partial_t \psi = K \int_r \tilde{A}_a + k_{11} r^2 \tilde{A}_a + k_{12} r^2 \pm C_a; \quad (13)$$

$$q \partial_t \phi = K \int_r \pm C_a + k_{21} r^2 \tilde{A}_a + k_{22} r^2 \pm C_a; \quad (14)$$

where ∇_r^2 is the Laplacian perpendicular to the normal of the particle surface. The coefficients k_{ij} are

$$\begin{aligned} Kk_{11} &= q^2 \int^{-1} + \frac{4C_0}{\int \cdot 2} \int; \\ Kk_{12} &= Kk_{21} = q\int^{-1} + \frac{4vC_0}{\int \cdot 2} \int + \frac{8C_0^2 q^3}{\int \cdot 3 T}; \\ Kk_{22} &= q^2 \int^{-1} + \frac{4C_0}{\int \cdot 2} \int + \frac{32C_0^2}{\int \cdot 3} \int \operatorname{cosh}^2 \frac{q^3}{4T}; \end{aligned} \quad (15)$$

In the above analysis, the tangential flow within the double layer depends weakly on the external flow, and hence can be solved without knowing the external flow. In the above expressions for k_{ij} , convection currents have been taken into account, in the terms contain the fluid viscosity η .

II-3-3. Monolayer charge

The surface charge can be redistributed on the monolayer. The perturbation of the monolayer charge ϕ_m obeys the conservation law

$$\frac{\partial \phi_m}{\partial t} = (K_m r^2 \frac{\partial \tilde{A}_a}{\partial t} + G r^2 \frac{\partial \phi_m}{\partial t}); \quad (16)$$

where G is the surface area compression modulus which characterizes the surface isotherm. In the dilute limit $\phi \rightarrow 0$, one expects $G = T$. The surface diffusivity G^1_m can be measured experimentally. Below, the monolayer conductivity is expressed as $K_m = q \phi^1_m$.

Assuming that $\phi_m / \cos \mu$, together with the form of the potential inside the emulsion $\tilde{A} = j E \phi r^{\tilde{A}}$, we solve ϕ_m in terms of \tilde{A} in Eq. (16) to give

$$\phi_m = j \frac{\omega^1}{\omega^1 + i} \frac{q \phi}{G} \tilde{A}_a - i C_m \tilde{A}_a \quad (17)$$

where $\omega^1 = 2G^1_m = a^2$. Note that the capacitance C_m , defined here, has dispersion around the frequency ω^1 .

The Gauss theorem gives

$$\phi + \phi_m = j \frac{\partial \phi}{\partial r} r \tilde{A}_a + \frac{\partial \phi}{\partial r} r \tilde{A}_a; \quad (18)$$

where the derivatives are evaluated outside the double layer and within the oil, respectively.

III. Result and discussion

III-1. The dipole strength

Equations (13), (14), (18), with ϕ , ϕ , and ϕ_m eliminated using (10), (11), (12), (17) provide three conditions to determine B , P , and \tilde{A} . The dipole strength P can be solved analytically, to obtain a very cumbersome expression (not shown) [13]. To simplify the analysis, we examine here the high ϕ^3 potential limit (where $j \frac{\phi}{\phi} \phi = q$). We replace k_{12} and k_{21} by k_{11} . The capacitances C_{11} , C_{22} are replaced by C_{12} . The high ϕ^3 dipole strength is :

$$P_3 = \frac{1}{2} i \frac{3}{2} \frac{k + \frac{i! C_d}{2K=a} \frac{C_m + C_o}{C_d + C_o + C_m}}{1 + (1 + \phi)k + \frac{i! C_d (C_m + C_o)(1 + \phi) + 2C_w}{2K=a} \frac{1}{C_d + C_o + C_m}} \quad (19)$$

where $k = k_{11} = a$, $\phi = \frac{1+a}{1+a+\frac{2}{a^2}}$, $C_d = C_{12} = q \phi = 2T$, $C_w = \frac{2}{\omega^2_w} = a$, $C_o = \frac{2}{\omega^2_{oil}} = a$. Using the De Lacey-White formula one can determinate ϵ_{eff} , which is shown in figure 2. In fact, the difference between the dielectric increments using Eq. (19) and the full expression is typically within a few percent [13]. Below, for the discussion purpose, we will only use Eq. (19).

There is an interfacial polarization dispersion for both charged and uncharged suspensions. The relaxation frequency is $K(1+k)(1+C_o=C_d) = \omega^2_w + \omega^2_{oil} = 2$. The known result of O'Brien [5] (for latex) can be recovered by taking the limit $C_d \rightarrow 1$.

Salt dispersion only appears for the charged suspensions. Similar to charged latex, the characteristic frequency $\omega_D = D = a^2$, is about one kHz for a micron size particle.

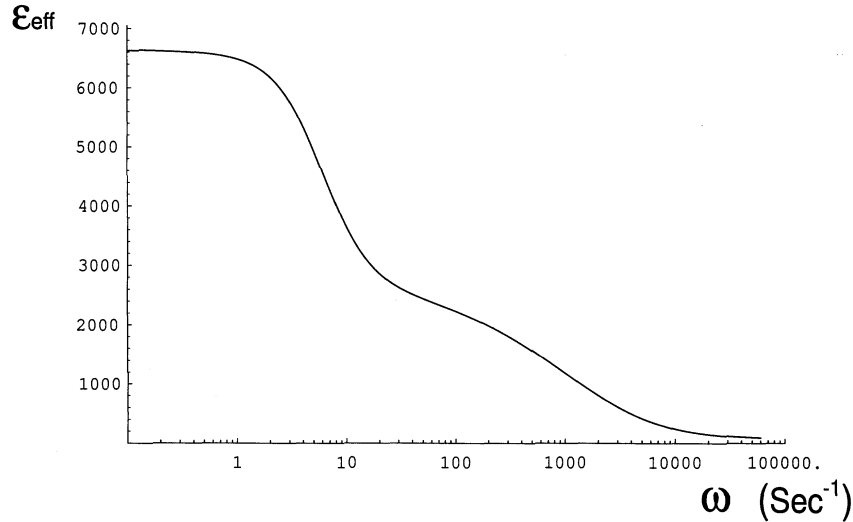


FIG. 2. The dielectric function $\epsilon_{eff}(\omega)$ of the emulsion solution, where $\bar{A} = 0.01$, $\xi = 0.16 \text{ C/m}^2$, $C_0 = 0.01\text{M}$, $a = 1 \mu\text{m}$, $D = 10^{-9} \text{ m}^2/\text{sec}$, $G_m = 10^{-12} \text{ m}^2/\text{sec}$. Given that the salt relaxation rate is 500 times the surface charge relaxation rate, the two dispersions are still not fully separated.

III-2. The surface charge relaxation

The surface charge relaxation is Debye-like, as shown in figure 3. The surface charge diffusion time $\tau_D = a^2/2G_m$, scales similarly as the salt diffusion time in the solution $\tau_D = a^2/D$. Therefore, for systems differing only in the droplet sizes, the ratio of these two relaxation rates $\tau_D = \tau_D$ is the same. If the surfactant (surface) diffusivity and the salt (bulk) diffusivity are of a similar order, it will be difficult to identify these two relaxations separately. In figure 2, even if the surface charge relaxation rate is 500 times smaller than τ_D , there is still no plateau between the two characteristic frequencies. This is due to the broad frequency dispersion of the salt relaxation.

The surface charge dielectric increment ϵ_{21} is defined as the zero frequency limit of ϵ_{eff} compared to the one of the fixed charge reference system (whose dipole strength is simply obtained by setting $C_m = 0$ in equation (19)). Within the high ω limit, the surface charge dielectric increment is

$$\epsilon_{21} = \frac{9}{4} \frac{\bar{A}^2 C_m}{\epsilon_0} \frac{1 + 2kC_w = C_d}{(1 + C_0 = C_d)(1 + C_0 = C_d + C_m = C_d)(1 + 2k)^2} \quad (20)$$

$$\approx \frac{9}{2} \frac{\bar{A}^2 \epsilon_0 \xi}{1 + \frac{\xi(1+\epsilon)}{qaC_0}} \frac{l_B a \xi = q}{2T + G} ;$$

where $l_B = q^2/4\epsilon_0^2 \epsilon_w T$ is the Bjerrum length. The effect of the convective current appears in $\pm \sqrt{4C_0} = \sqrt{1 + 2k}$ (from k). The capacitances C_0 and C_w are much smaller than the double layer capacitance C_d so that we have to neglect the terms contain C_0 and C_w in the last expression.

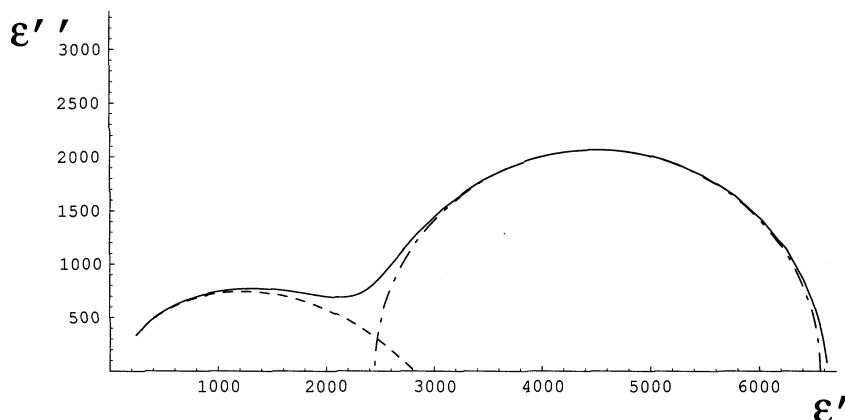


FIG. 3. The Cole-Cole plot of the emulsion solution, where $\epsilon''(\omega) = \epsilon''_{eff}(\omega)$, $\epsilon''(0) = (K_{eff}(\omega) - K_{eff}(0)) = \epsilon''_0$. The parameters are as in Figure 2. The dashed line is the reference system with fixed surface charge. The dot dash line is a fitted semicircle, to illustrate that the surface charge relaxation is almost Debye-like.

It is interesting to note that there is no contribution from $P^0(\omega \neq 0)$ (the real part), which is the same as in the reference system. This means that the static dipole close to or within the emulsion does not depend on the surface charge relaxation. The surface charge redistribution will always be accompanied by the double layer readjustment, so that the net dipole contribution stays the same. In dynamics, the distorted surface charge is not completely screened by the polarized double layer. The residual transient dipole field charges up the system by accumulating charges close to the electrodes [14].

For a rigid monolayer (large G), the surface charge polarization is weak. The dielectric increment ϵ''_1 is inversely proportional to the modulus G . For a very compressible monolayer $G \ll T$, the dielectric increment ϵ''_1 actually gets saturated.

For a large droplet, $a > a_0 \approx \xi(1 \pm) = qC_0$, the dielectric increment is linearly proportional to a (for fixed volume fraction \bar{A}). This might be a useful tool for monitoring the coarsening dynamics of the dilute emulsions. For very small droplets, $a \ll a_0$, the dielectric increment is proportional to a^3 . For fixed surface charge density, ϵ''_1 is proportional to C_0^2 at smaller salt concentration, and saturated when $C_0 \bar{A} \approx \xi = qa$.

When the surface charge is small, the dielectric increment ϵ''_1 increases with the surface charge. However, the dielectric increment assumes the maximum value when $\xi = \xi_{max} \approx qaC_0 = (1 + 1/(2\epsilon_0 \epsilon_B))$ which is linearly proportional to the droplet radius and the salt concentration. For $C_0 = 0.005$ M, $a = 1 \mu\text{m}$, ϵ''_1 has a maximum value at $\xi = 0.289$ C/m² (one charge per 55 Å²). This reduction at high surface charge is due to the progressively large surface conductance, which tends to reduce the dipole contribution.

One notices that Eq. (20) is similar to Schwarz's results [11]. Schwarz's theory was originally proposed to model the double layer polarization effect. We have accounted for that effect by the standard double layer polarization theory (salt relaxation). Except for neglecting the salt relaxation, Schwarz's theory neglects the double layer structure ($k \neq 0$ and $C_d \neq 1$), and

assumed a 2D ideal gas compressibility $G = T$. The finite $C_d = q^2/\epsilon_0 = 2T$ corrects Schwarz's result to one third of it. The finite k reduces it further. Therefore Schwarz's result, interpreted as the surface charge relaxation, overestimated the dielectric increment (by a factor of three or more).

In summary, we have presented an unified theory of the dielectric response of a dilute O/W charged emulsion solution. The high ϕ potential result is given explicitly, and the method can be applied for the full range of the ϕ potential. Our single formula bridges previous limiting results on Maxwell-Wagner relaxation for dielectric sphere [5], and salt relaxation [8, 10]. The surface charge relaxation, which is unique to emulsion droplets, is Debye-like. The surface charge dispersion is likely to partially overlap with the salt diffusion relaxation. The surface charge dielectric increment can have a large value, and does not always increase with the surface charge.

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*Electronic address: dlu@phy.ncu.edu.tw

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