

Electroacoustic Phenomena in Concentrated Dispersions: Effect of the Surface Conductivity

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In our previous paper,¹ we have derived a new electroacoustic theory for concentrated (up to 45 vol%) polydisperse colloids. We assumed two simplifications: thin double layer and negligible surface conductivity. In this paper, we generalize this theory eliminating the second assumption by taking into account the surface conductivity influence on the electroacoustic CVI signal.

Introduction

There are two quite different approaches to deriving an electroacoustic theory. Historically the first began with works by Enderby and Booth.^{2,3} They simply tried to solve a system of classical electrokinetic equations without using any thermodynamic relationships. It was very complex because they took into account surface conductivity and concentration polarization effects. Although this initial theory was valid only for dilute systems, this approach was later expanded by Malrow, Fairhurst, and Pendse,⁴ who tried to generalize it for concentrated systems using a Levine cell model⁵ which is not appropriate for this purpose.⁶

An alternative approach to electroacoustic theory was suggested later by O'Brien.^{12,13} He introduced the concept of a dynamic electrophoretic mobility μ_d and suggested a

relationship between this parameter and the measured electroacoustic parameters such as colloid vibration current (CVI) or electrosonic amplitude (ESA).

We used the first approach in our previous paper for deriving theory based on the "coupled phase model"⁷⁻¹⁰ and Shilov-Zharkikh cell model.¹¹ This new electroacoustic theory has been developed so far only for the case of thin double layer and negligible surface conductivity. It is sufficient for many real dispersed systems including ones which were used for dilution tests. The existing version of this theory somewhat resembles Smoluchowski theory for microelectrophoresis which is valid at the same set of conditions. This analogy is especially strong at low frequency where effect of the particle size on the electroacoustic signal disappears. At this limit, the new electroacoustic theory gains a very important feature of the Smoluchowski theory, the electroacoustic signal is independent of the particle shape.

However, it is known from the classical electrophoresis theory that Smoluchowski theory is valid only when surface conductivity is low, which is expressed as the condition of a small "Dukhin number"¹⁷

$$Du = \frac{\kappa^s}{K_m a} \ll 1 \quad (1)$$

where κ^s is the surface conductivity, K_m is a bulk conductivity of the equilibrium medium, and a is a particle radius. There are several electrophoretic theories¹⁸⁻²²

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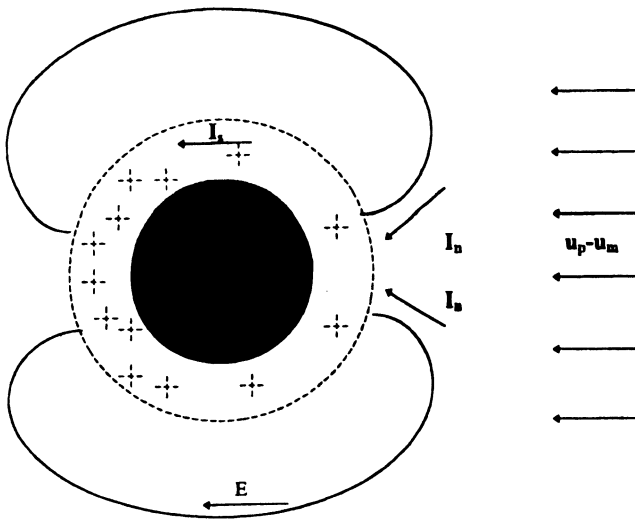


Figure 1. Mechanism of the double layer polarization generating sedimentation current for a single particle.

which are more general than Smoluchowski theory because they take into account surface conductivity effects. This generalization turns out to be important for some real dispersions.¹⁷ Following the same path, we should develop a more general version of the electroacoustic theory which would take into account surface conductivity effects. To do this, we must modify our description of the surface current. In our previous paper, we considered only one cause of this current, liquid motion relative to the particle surface. We should add now an electrodynamic component to the existing hydrodynamic term. It is done in this paper.

Theory

We have used before an analogy between colloid vibration current and sedimentation current which is well-known from classical colloid chemistry.^{17,23,24} Simply put, charged particles sediment due to gravity will develop a sedimentation potential between two vertically spaced electrodes. If we externally short circuit these electrodes, the current which flows is referred to as sedimentation current. We can extend this simple concept to include colloid vibration current by simply replacing the acceleration of gravity with analogous acceleration caused by the applied acoustic field. This idea is described in more detail in the last section.

Figure 1 illustrates a particle with a double layer moving relative to the liquid. This motion involves ions of the double layer. In this case, we consider only the positive counterions opposing the negative charged particle surface. The hydrodynamic surface current I_s reduces the number of the positive ions near the right particle pole and enriches the double layer with extra ions near the left pole. As a result, the double layer shifts from the original equilibrium. The negative surface charge dominates at the right pole, whereas extra positive diffuse charge dominates at the left pole. The net result is that the motion has induced a dipole moment.

This induced dipole moment generates an electric field which is usually referred to as a colloid vibration potential (CVP). This CVP is external to the particle double layer. It affects ions in the bulk of the electroneutral solution

beyond the double layer generating electric current I_n . This electric current serves a very important purpose. It compensates for the surface current I_s and makes the whole picture self-consistent.

The next step is to add a quantitative description to this simple qualitative picture. To do this we must find a relationship between the CVP and the speed of the relative motion particle and liquid ($u_p - u_m$). We did this in our previous paper¹ assuming that the double layer thickness must be much smaller than particle radius a :

$$\kappa a \gg 1 \quad (2)$$

where κ is reciprocal Debye length.

It is possible to eliminate this restriction in the future following well-known papers by Babchin et al.^{26,27} The second simplification required a surface conductivity κ'' contribution to be negligible. It happens when the dimensionless Dukhin number Du introduced by Lyklema¹⁷ is sufficiently small. In this paper, we are going to eliminate the second simplification and derive theory which takes into account surface conductivity. We will do this for the frequencies ω which are below the Maxwell-Wagner frequency ω_e ,

$$\omega \ll \omega_e = \frac{K_m}{\epsilon \epsilon_0} \quad (3)$$

where K_m is a conductivity of the medium and ϵ_0 and ϵ are the dielectric permittivity of the vacuum and medium.

The condition of the thin double layer allows us to describe the distribution of the electric potential ϕ with the Laplace equation

$$\Delta \phi = 0$$

The general spherical symmetrical solution of this equation

$$\phi = -Er \cos \theta + \frac{d}{r^2} \cos \theta \quad (4)$$

contains two unknown constants E and d . Two boundary conditions are required for calculating these constants.

The surface boundary condition reflects continuity of the bulk current I and surface current I_s ,

$$K_m \nabla_n \phi = \text{div}_s I_s \quad (5)$$

In our previous work, we considered only hydrodynamic component of the surface current neglecting electrodynamic contribution associated with the surface conductivity. In this paper, we take into account both components, which leads to the following expression for the surface current:

$$I_s = -\epsilon \epsilon_0 \zeta \frac{\partial u_\theta}{\partial r_{r=a}} - \kappa'' \frac{1}{a} \frac{\partial \phi}{\partial \theta_{r=a}} \quad (6)$$

Substitution of the eq 6 into eq 5 yields the first boundary condition,

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$$\left(\frac{2\kappa^0}{a} - K_m\right)E - \left(\frac{2\kappa^0}{a} + 2K_m\right)\frac{d}{a^3} = -\frac{1}{a}\epsilon\epsilon_0\zeta\frac{1}{\sin\theta}\frac{\partial u_\theta}{\partial r_{r=a}} \quad (7)$$

We will use the cell model concept for deriving the second boundary condition. According to this concept, we equally redistribute liquid between particles and assume that liquid associated with each particle creates a spherical cell of the radius b . This radius is related with the particle radius according to the following expression:

$$b^3 = \frac{a^3}{\varphi} \quad (8)$$

We prefer to use the Shilov–Zharkikh cell model¹¹ over the Levine one.⁵ All arguments for this decision are given in ref 6. These two cell models yield the different expressions for the macroscopic electric field $\langle E \rangle$:

$$\langle E \rangle_{\text{levine}} = \frac{1}{\cos\theta} \frac{\partial\phi}{\partial r_{r=b}}$$

$$\langle E \rangle_{\text{shilov}} = \frac{\phi}{b \cos\theta_{r=b}}$$

Cell boundary condition specifies the values of the normal derivative of the electric potential on the cell surface. In the Shilov–Zharkikh cell model it equals

$$\frac{\partial\phi}{\partial r_{r=b}} = \frac{\phi_{r=b}}{b \cos\theta} = -E + \frac{d}{b^3} = 0 \quad (9)$$

To find CVP, we should calculate unknown constants E and d using eq 7 and eq 9 and substitute this result into the following expression for the colloid vibration current:

$$\text{CVI} = \frac{I_r(r=b)}{\cos\theta} = -\frac{K_m \frac{\partial\phi}{\partial r_{r=b}}}{\cos\theta} = K_m \left(E + \frac{2d}{b^3} \right) \quad (10)$$

As a result, we obtain the following relationship between CVI and tangential fluid velocity:

$$\text{CVI} = \frac{3\varphi}{\left(\frac{\kappa^0}{K_m a} + 1\right) - \left(\frac{\kappa^0}{K_m a} - 0.5\right)\varphi} \frac{\epsilon\epsilon_0\zeta}{a} \frac{1}{\sin\theta} \frac{\partial u_\theta}{\partial r} \quad (11)$$

This expression has been derived for the monodisperse system. Let us assume now that we have polydisperse system with conventional N fractions. Each fraction of particles has certain particle radius a_i , volume fraction φ_i , drag coefficient γ_i , and particle velocity u_i in the laboratory frame of references. We assume density of the particles to be the same for all fractions ρ_p as well as surface conductivity κ^0 and ζ -potential. The total volume fraction of the dispersed phase is φ . Liquid is characterized by dynamic viscosity η , density ρ_m , and velocity in the laboratory frame of references u_m . Generalization of the cell model concept for the polydisperse system which is described in refs 1 and 9 yields the following relationship between the fractional particle radius and the radius of the shell b_i :

$$b_i^3 = \frac{b_i^3}{\varphi} \quad (12)$$

equals

$$\text{CVI}_i = \frac{3\varphi_i}{\left(\frac{\kappa^0}{K_m a_i} + 1\right) - \left(\frac{\kappa^0}{K_m a_i} - 0.5\right)\varphi} \frac{\epsilon\epsilon_0\zeta}{a_i} \frac{1}{\sin\theta} \frac{\partial u_{i\theta}}{\partial r_{r=a_i}} \quad (13)$$

The radial derivative from the tangential velocity had been calculated in our previous paper¹,

$$\frac{1}{\sin\theta} \frac{\partial u_{i\theta}}{\partial r_{r=a_i}} = \frac{3(u_{ip} - u_m)h(\alpha_i)}{I(\alpha_i)} \quad (14)$$

where h and I are special functions given in Appendix 2.

The coupled phase model allows us to calculate the difference $u_i - u_m$ for each fraction without using the superposition assumption:¹

$$u_i - u_m = \frac{\left(\frac{\rho_p}{\rho_m} - 1\right)\nabla P}{\left(j\omega\rho_p + \frac{\gamma_i}{\varphi_i}\right) \left(1 + \frac{\rho_p}{(1-\varphi)\rho_m} \sum_{i=1}^N \frac{\gamma_i}{j\omega\rho_p + \frac{\gamma_i}{\varphi_i}}\right)} \quad (15)$$

where

$$\gamma_i = \frac{9\eta\varphi_i\Omega}{2a_i^2}$$

$$F_{\text{stockes}}^i = 6\pi\eta a\Omega(u_i - u_m)$$

The values of the special functions $h(x)$ and $I(x)$ are presented in Appendix 2.

We can use eq 15 for calculating speed of the liquid motion relative to the particle surface only if we neglect electroosmotic flow caused by CVP. This electroosmotic flow is a secondary effect, but it would still need justification for being neglected. This is done in Appendix 1, where we show that the electroosmotic flow is reciprocally proportional to $(\kappa a)^2$.

The final expression for CVI can be obtained as a sum of the fractional currents generated by the fractional dipole moments. This expression is

$$\text{CVI} = \frac{9\epsilon\epsilon_0\zeta(\rho_p - \rho_m)\nabla P}{4\eta} \frac{\sum_{i=1}^N \frac{1}{(Du_i + 1) - (Du_i - 0.5)\varphi} \frac{\varphi_i H(\alpha_i)}{j\alpha_i I(\alpha_i) \left(\rho_p - \rho_m \left(\frac{3H_i}{2I_i} + 1\right)\right)}}{1 - \frac{\rho_p}{1-\varphi} \sum_{i=1}^N \frac{\varphi_i \left(\frac{3H_i}{2I_i} + 1\right)}{\rho_p - \rho_m \left(\frac{3H_i}{2I_i} + 1\right)}} \quad (16)$$

where $\alpha = a\sqrt{\omega/2\nu}$, $\beta = ba/a$, ν is the kinematic viscosity,

the pressure and frequency of the ultrasound, and special functions h , H , and I are given in the Appendix 2, $H_i = H(\alpha_i)$, $I_i = I(\alpha_i)$.

According to the assumption of the monodisperse surface conductivity, the value of the fractional Dukhin number equals

$$Du_i = \frac{\kappa^\sigma}{K_m a_i} \quad (17)$$

This expression can be easily converted to the formulas from the previous paper if we neglect terms with the Dukhin number and use Maxwell–Wagner theory for conductivity²⁵

$$\frac{K_s}{K_m} = \frac{1 - \varphi}{1 + 0.5\varphi} \quad (18)$$

Discussion

Equation 16 describes the electroacoustic effect only below the Maxwell–Wagner critical frequency (see eq 5). This assumption restricts electrolyte concentration range for the given frequency of the particular measurement. For instance, if we measure CVI at 1 MHz, eq 18 is applicable for electrolyte concentrations which exceed 0.001 mol/L.

The condition of the thin double layer (eq 2) is also related to the concentration of electrolyte. For the given concentration, it determines the minimum size of the particles. In general, assumption of the thin double layer is valid when

$$\kappa a > 20$$

This condition limits the particle size range to be above 200 nm for the electrolyte concentration 0.001 mol/L. In the case of the higher ionic strength, the particle size range expands. For instance, in the case of 0.1 mol/L, eq 18 works for particles above 20 nm in size.

To characterize the surface conductivity influence, we suggest using the following parameter:

$$\frac{CVI(Du=0) - CVI}{CVI(Du=0)}$$

which compares the CVI value according to the eq 16 with CVI at zero surface conductivity ($Du = 0$). Figure 2 illustrates graphically the dependence of this parameter on the Dukhin number for dispersion with 10 vol% of the particles with 1 μm median size, 0.2 standard deviation, density of particles is 3 g/cm³, density of the liquid 1 g/cm³.

It is seen that contribution of the surface conductivity exceeds 10% as Dukhin number becomes larger than 0.1. We suggest considering this value $Du = 0.1$ as a critical point for characterizing importance of the surface conductivity. In the case of $Du < 0.1$, we can neglect surface conductivity effects. The possible error in the calculated value of ζ -potential will not exceed 10%.

It is interesting to estimate the contribution of the surface conductivity in terms of ζ -potential instead of the Dukhin number. For this purpose, we need a functional relationship between ζ -potential and the Dukhin number. There are several different expressions suggested by various authors. Appendix 3 gives the simplest one (eq 3.1) and the most complicated one (eq 3.2). This most complicated expression is the most adequate because it takes into account surface conductivity under the slipping

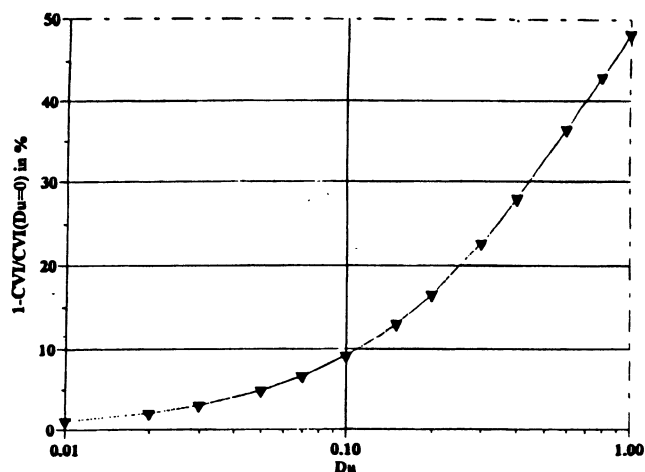


Figure 2. Theoretically calculated difference between CVI (eq 16) and CVI at $Du = 0$ versus Dukhin number for dispersion with 10 vol% of 1 μm particles with a standard deviation of 0.2. Density of the liquid is 1 g/cm³; that of the particles is 3 g/cm³; the frequency is 1 MHz.

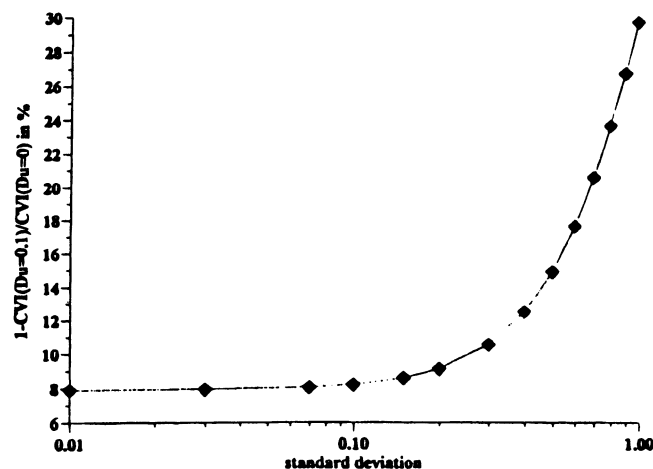


Figure 3. Theoretically calculated difference between CVI ($Du = 0.1$) and CVI ($Du = 0$) versus standard deviation for dispersion with 10 vol% of 1 μm particles. Density of the liquid is 1 g/cm³; that of the particles is 3 g/cm³; the frequency is 1 MHz.

Table 1. Values of the ζ -Potential Which Yields a Dukhin Number Equal to 0.1 for the Particular Values of κa

ζ [mV]	36	57	71	83	92	100	106	112	118
κa	20	30	40	50	60	70	80	90	100

it contains two more unknown parameters: Stern potential and anomalous surface conductivity. That is why we suggest using the simplest form, eq 3.1. The corresponding values of ζ -potential are given in the Table 1. Surface conductivity is not important if ζ -potential is smaller than the number given in Table 1 for the particular κa . However, we should keep in mind that anomalous surface conductivity may change this conclusion and make surface conductivity effects important even at smaller ζ -potentials.

In addition, the contribution of the surface conductivity depends on the polydispersity of the particle size distribution. Figure 3 illustrates this dependence for the same dispersion as for Figure 2 and $Du = 0.1$. It is seen that for wide particle size distributions surface conductivity is more important because of the larger content of the small particles. Conclusions formulated above are valid only for

Conclusions

We have derived a more general version of the new electroacoustic theory which does not use O'Brien's relationship between electroacoustic signal and dynamic electrophoretic mobility. This new version does take into account surface conductivity effect. As a result, it is supposed to be valid for all polydisperse concentrated dispersions with a thin double layer.

Appendix 1: Electroosmotic Contribution

Electric field associated with the electroacoustic effect creates additional electroosmotic flow of the liquid relative to the particle surface. Let us denote the value of this flow speed as u_{el} . We neglected u_{el} comparing to the $(u_p - u_m)$ which was yielded by the coupled phase model. Is it justified?

To answer this question we should calculate u_{el} which is done here. Electroosmotic flow is potential in the case of the thin double layer

$$u = -\text{grad } A \quad (1.1)$$

$$A = -Vr \cos \theta + \frac{d_v}{r^2} \cos \theta \quad (1.2)$$

In addition, we can use the following boundary conditions:

$$u_r(r=a) = 0 \quad (1.3)$$

$$u_\theta(r=a) = -\frac{\epsilon\epsilon_0\zeta}{\eta} E_\theta = -\nabla_\theta A \quad (1.4)$$

The average speed of the electroosmosis u_{el} equals the value of the local liquid speed on the surface of the cell,

$$u_{el} = \frac{u_r(r=b)}{\cos \theta} \quad (1.5)$$

We can calculate the value of the potential A from the eqs 1.2–1.4:

$$A = \frac{2\epsilon\epsilon_0\zeta}{3\eta} \frac{E_\theta(r=a)}{\sin \theta} \left(r + \frac{a^3}{2r^2} \right) \cos \theta \quad (1.6)$$

where E_θ is a tangential component of the electric field (eq 4),

$$E_\theta(r=a) = -\nabla_\theta \phi(r=a) - \left(E - \frac{d}{a^3} \right) \sin \theta \quad (1.7)$$

Values of the constants E and d can be taken from the given above theory. As a result, we have the following expression for u_{el} :

$$u_{el} = \frac{2}{3} \frac{(\epsilon\epsilon_0\zeta)^2}{\eta a K_m} \frac{(1-\varphi)^2}{\left(\frac{\kappa''}{K_m a} + 1 \right) - \left(\frac{\kappa''}{K_m a} - 0.5 \right) \varphi} \frac{1}{\sin \theta} \frac{\partial u_\theta}{\partial r} \quad (1.8)$$

At this point, we can use eq 14 in order to introduce the $(u_p - u_m)$. As a result, we have the following estimate for electroosmotic contribution:

$$\frac{u_{el}}{u_p - u_m} \cong \frac{(\epsilon\epsilon_0\zeta)^2}{\eta} \frac{1}{K_m a^2} = m \zeta^2 \frac{1}{(\kappa a)^2} \quad (1.9)$$

$$m = \frac{2\epsilon\epsilon_0(RT)^2}{\eta D F^2}$$

$$\zeta = F\zeta/RT$$

where F is Faraday number, R is a gas constant, T is the absolute temperature, and D is effective diffusion coefficient.

This expression confirms that electroosmotic contribution is small within the adopted scope of the thin double layer assumption eq 2.

Appendix 2: Special Functions

There are several special functions used in this theory. They are specified in this section.

$$H(\alpha) = \frac{ih(\alpha)}{2\alpha} - \frac{idh(x)}{2dx} \Big|_{x=\alpha}$$

$$h(x) = h_1(x)h_2(\beta) - h_1(\beta)h_2(x)$$

$$I = I(\beta) - I(\alpha)$$

$$I(x) = I_1(x) - I_2(x)$$

$$I_1(x) =$$

$$- h_1(\beta) \exp(x(1+i)) \left[\frac{3(1-x)}{2\beta^3} + i \left(\frac{x^2}{\beta^3} - \frac{3x}{2\beta^3} - \frac{1}{x} \right) \right]$$

$$I_2(x) =$$

$$- h_2(\beta) \exp(-x(1+i)) \left[\frac{3(1-x)}{2\beta^3} + i \left(\frac{x^2}{\beta^3} - \frac{3x}{2\beta^3} - \frac{1}{x} \right) \right]$$

$$h_1(x) =$$

$$\frac{\exp(-x)}{x} \left[\frac{x+1}{x} \sin x - \cos x + i \left(\frac{x+1}{x} \cos x + \sin x \right) \right]$$

$$h_2(x) =$$

$$\frac{\exp x}{x} \left[\frac{x-1}{x} \sin x - \cos x + i \left(\frac{1-x}{x} \cos x + \sin x \right) \right]$$

Appendix 3: Various Approximations for Dukhin Number

There are several different relationships between Dukhin number and parameters of the double layer depending on the DL model.²⁸ For instance, the Australian school^{12,13,20–22} uses the simplest DL model assuming equality of the Stern potential and ζ -potential. Their version of the Dukhin number of the symmetrical electrolyte is the following:

$$Du = \left(1 + \frac{3m}{z^2} \right) \frac{\exp(zF\zeta/2RT)}{\kappa a} \quad (3.1)$$

This approximation is not adequate because surface conductivity almost always exceeds values calculated assuming simple Gouy–Chapman DL model (see review²⁸). For instance, Midmore and Hunter wrote in the paper:²⁹ "This treatment assumes no contribution to the electric conduction by any Stern layer ions and that the Poisson–Boltzmann equation applies up to the outer

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Helmholtz plane. The diffuse layer ions between the shear plane (where ζ is measured) and the outer Helmholtz plane (where Stern potential ψ is measured) do conduct a current and this anomalous surface conduction (inside the shear plane) dramatically reduces the mobility for a given value of ζ ...".

Another approach has been promoting by S. Dukhin and his colleagues.^{11,17-19,25,28} They suggest to consider the more general DL model (Stern model) and take into account electric conductance under the slipping plane and even, perhaps, within the surface layer. The most general

expression for the Dukhin number is the following:

$$Du = \frac{2}{\kappa a} \left(ch \frac{z\tilde{\Psi}}{2} - 1 + 6msh \frac{2z\tilde{\zeta}}{2} \right) + 2862 \frac{\kappa^{sa} a (z^+ - z^-)}{zD(\kappa a)^2} \quad (3.2)$$

where κ^{sa} is the anomalous surface conductivity.

Expression 3.2 is certainly more general but it contains more unknowns compared to the expression 3.1. The way to determine these unknowns is described in the review.²⁸

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