Frequency–Dependent Electro–Osmosis

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I. Introduction

Electro-osmosis, the movement of a fluid with respect to a solid wall when an electric field is applied tangentially to the solid wall, has been studied for many years\(^1\). Frequency-dependent electro-osmosis (FDE), the study of electro-osmosis when the applied electric field has a frequency component has only recently been studied\(^2\). There are many potential reasons for studying frequency-dependent electro-osmosis ranging from medicine to geophysics. In medicine, electro-osmosis has been used to study a variety of human processes\(^3,4\). However, new areas of study may be related to electro-osmosis effects on the bodies, such as: electrical workers working in close proximity to high voltage AC electromagnetic fields, or the effects of cellular EM waves on human brains.

In the geosciences, there has been recent interest in streaming potentials as related to earthquake phenomena\(^5,6\). There has also been recent work, which suggests that frequency-dependent streaming potentials may be useful for determining the permeability of rocks\(^7,8\). FDE's counterpart, frequency-dependent streaming potentials, has been shown useful in determining capillary diameters and the pore diameters of porous media\(^8,9\). This leads to another reason for studying FDE, which is the potential for using FDE to study fluid flow in capillaries and porous media.

Frequency-dependent electro-osmosis may have significant advantages over frequency-dependent streaming potentials for the study of fluid flow, due to the
differences in the cross-coupling coefficient properties of both phenomena. The streaming potential coupling coefficient is the ratio of the measured streaming potential voltage to the pressure applied across the sample \((\Delta V_{m}/\Delta P_{a})\), where the subscripts “m” and “a” stand for the measured and applied, respectively. The frequency-dependent streaming potential coupling coefficient decreases as the frequency is increased past the critical frequency, implying that the induced voltage decreases relative to the pressure applied across the sample. This situation can be problematic in the approximate frequency range of 500 Hz to 10 kHz. In this frequency range, pressure-generating devices are very inefficient, making it difficult to generate pressures large enough to induce measurable streaming potential signals. Therefore, in the frequency range of 500 Hz to 10 kHz, FDE may be more useful than frequency-dependent streaming potentials because \(\Delta V\) is applied and \(\Delta P\) is measured in the FDE case. Due to the nature of the signals, it is much easier to generate large amplitude voltage signals than it is to generate large amplitude pressure signals at high frequencies.

The frequency-dependent electro-osmosis coupling coefficient is the ratio of the voltage applied across the sample to the induced pressure measured across the sample \((\Delta V_{s}/\Delta P_{m})\). It has been found in this research that the FDE coupling coefficient, like the frequency-dependent streaming potential coupling coefficient, decreases as the frequency is increased past the critical frequency. There is a significant difference however, between the streaming potential and the electro-osmosis cases. In the frequency-dependent electro-osmosis case, the voltage applied across the sample can be kept constant in magnitude; this implies that the pressure measured across the sample
increases as the frequency is increased past the critical frequency. This has practical implications, which will make measurement of the pressure easier at the higher frequencies.

Until recently, little attention has been paid to frequency-dependent electro-osmosis. Minor et al.\textsuperscript{2} determined the characteristic time for dynamic electro-osmosis and electrophoresis. Electrophoresis being related to electro-osmosis in that the fluid remains stationary while the electric field causes colloidal particles to move tangential to the applied electric field. Minor et al.\textsuperscript{2} provided data showing the relaxation frequency and then fitted the data with an empirically determined curve using the characteristic time. According to Minor et al.\textsuperscript{2}, there was not a good correlation between the theoretical and measured relaxation frequencies, although the general shape of the curves was in good agreement. Recently there have been other papers on frequency-dependent/dynamic electrophoresis\textsuperscript{10,11}, but they do not provide analytical solutions for the mobility. In the study of electro-osmosis, the term mobility refers to $-\varepsilon \zeta / \eta$, where $\varepsilon$ is the permittivity of the fluid, $\zeta$ is the zeta potential, and $\eta$ is the viscosity of the fluid.

This paper provides the theoretical development of an analytical solution for frequency-dependent electro-osmosis in a capillary. First a brief review of DC electro-osmosis is presented, followed by the theory of frequency-dependent electro-osmosis. Furthermore, experimental data collected by the authors are presented to verify the theory.
II. Theory of DC Electro-osmosis

DC electro-osmosis has been studied in its present form, since originally presented by von Smoluchowski in 1921\textsuperscript{12}. In DC electro-osmosis an electric field is applied tangentially to a charged surface in contact with an ionic fluid, causing the fluid to move parallel to the surface. The fluid is moved by the electric field through its affect on the ions in the diffuse layer of the electrical double layer, which is adjacent to the surface. A simplified schematic representation of the Stern\textsuperscript{13} model of the electrical double layer is shown in Fig. 1. The zeta ($\zeta$) potential is the potential at the slipping plane (S), the potential at the surface is $\varphi_o$, and $\varphi_d$ is the potential at the Stern plane (OH). It can be seen in Fig. 1 that the potential decays exponentially from the Stern layer into the bulk fluid. This implies that there is excess charge near the Stern layer. Consequently, as the electric field moves the ions, viscous effects in the fluid near the surface pull the fluid along with the ions. This can be seen in Fig. 2, which is a modified version of Hunter’s\textsuperscript{12} figure. For a planar surface where the electric field is applied tangential to the surface, the equation governing DC electro-osmosis is

\[
\eta \frac{d^2 u_x}{dx^2} = -E_x \rho_c \tag{1}
\]

where $E_x$ is the electric field applied tangentially to the surface, $\rho_c(x)$ is the charge density, $\eta$ is the viscosity of the fluid, $u_x(x)$ is the DC electro-osmotic fluid velocity, and “$x$” is the distance from the surface. Applying Poisson’s equation to substitute for $\rho_c(x)$, Eq. (1) can be rewritten as

\[
\eta \frac{d^2 u_x(x)}{dx^2} = -E_x \varepsilon \frac{d^2 \varphi(x)}{dx^2} \tag{2},
\]

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where \( \phi(x) \) is the potential, and \( \varepsilon \) is the permittivity of the fluid. Solving this differential equation with the boundary conditions that \( d\phi/dx = 0 \) and \( du_z/dx = 0 \) in the bulk fluid and \( \phi = \zeta \), and \( u_z = 0 \) at the surface gives

\[
    u_z(x) = \frac{\varepsilon}{\eta} E_z \left[ \phi(x) - \zeta \right] .
\]

(3)

With the substitution of the Debye-Hückel approximation, \( \phi(x) = \zeta \exp(-\kappa x) \), for the potential distribution, Eq. (3) becomes

\[
    u_z(x) = \frac{\varepsilon \zeta}{\eta} E_z \left[ \exp(-\kappa x) - 1 \right] ,
\]

(4)

which is often approximated by

\[
    u_z = -\frac{\varepsilon \zeta}{\eta} E_z .
\]

(5)

This approximation holds at a distance of three Debye lengths and greater from the wall where the velocity is essentially a constant. This can be seen by plotting Eq. (4), as shown in Fig. 3, where the constant velocity is achieved at approximately \( 3/\kappa \), and \( 1/\kappa \) is the Debye screening length. The Debye screening length is the distance at which the charge potential is reduced by a factor of 2.718 (e) and is given by \( 1/\kappa \), where \( \kappa \) is the Debye-Hückel parameter whose linear approximation is given by

\[
    \kappa = \left( \frac{10^3 \left( 2z^2 e^2 I_r N_A \right)}{\varepsilon k_B T} \right)^{1/2} ,
\]

(6)

where \( z \) is the valence of the ions, \( e \) is the charge of an electron, \( I_r \) is the ionic strength of the fluid, \( N_A \) is Avogadro’s constant, \( k_B \) is Boltzmann’s constant and \( T \) is the temperature.
in Kelvins. The approximation made in Eq. (5) holds because in electro-osmosis fluid volumes are often the primary concern. The fluid volume within three Debye lengths of the wall is infinitesimal compared to the volume in the bulk fluid, provided that the capillary radius is large compared to the Debye length. Consequently, the bulk fluid response controls the volume response.

In a closed capillary, the electro-osmotic flow induces a pressure gradient. The pressure gradient generates a back flow whose volume flow must balance the electro-osmotic volume flow. This is seen schematically in Fig. 2b, which shows the electro-osmosis flow and the counter-flow. The electro-osmosis DC coupling coefficient is found by setting the electro-osmosis volume flow equal to the counter volume flow and taking the ratio $\Delta V/\Delta P$, which gives

$$\frac{\Delta V}{\Delta P} = \frac{x^2}{8\varepsilon \zeta}.$$  \hspace{1cm} (7)

III. Theory of Frequency-Dependent Electro-osmosis

Having done a brief review of DC electro-osmosis, frequency-dependent electro-osmosis will now be examined. Using the same boundary conditions where an electric field is applied tangentially to a surface in contact with an ionic fluid, the force balance equation governing frequency-dependent electro-osmosis is

$$\rho \frac{\partial}{\partial t} [\psi_z(x) e^{i(\omega t + \theta)}] = \eta \frac{\partial^2}{\partial x^2} [\psi_z(x) \exp[i(\omega t + \theta)]] - \varepsilon \frac{\partial^2 \phi(x)}{\partial x^2} E_z \exp[i\omega t]$$ \hspace{1cm} (8)
where $E_x \exp(i\omega t)$ is the sinusoidal forcing function and $\nu_z(x)\exp[i(\omega t + \theta)]$ is the sinusoidal response with an unknown phase ($\theta$) and $\rho$ is the density of the fluid. Introducing phasor notation into the problem, which is often used in electrical engineering,

$$\mathbf{v} = \nu_z \exp[i(\omega t + \theta)] = w + iy,$$

where $\nu_z$ is a real vector, and $\mathbf{v}$ is a complex vector with a real component $w = \text{Re}(\mathbf{v})$ and imaginary component $y = \text{Im}(\mathbf{v})$. After taking the derivative with respect to time of the left side of Eq. (8), and using phasor notation, which takes the Fourier transform and allows the equation to be viewed in the frequency domain, Eq. (8) can now be represented as

$$i\rho \omega \mathbf{v}(x, \omega) = \eta \frac{\partial^2 \mathbf{v}(x, \omega)}{\partial x^2} - \varepsilon \frac{\partial^2 \varphi(x)}{\partial x^2} \mathbf{E}(\omega).$$

(10)

This equation is essentially a modified form of the Navier-Stokes equation,

$$\rho \frac{\partial \mathbf{v}}{\partial t} = \eta \nabla^2 \mathbf{v} + \mathbf{B} - \nabla P,$$

(11)

where the first term of Eq. (8 & 10) is the fluid density multiplied by the acceleration of the fluid to give the inertial forces, which equates to the first term of Eq. (11). The second term of Eq. (8 & 10) represents the viscous forces in the fluid, which equates to the second term of Eq. (11), which are also the viscous forces. The third term of Eq. (8 & 10) represents the forces due to the electric field. This term equates to the third term in Eq. (11) which are the body forces on the fluid. The last term in Eq. (11), the pressure gradient, does not appear in Eq. (8 & 10) because the solution is for an open capillary. It
can be seen in the earlier development of DC electro-osmosis in this paper or in the
development of DC electro-osmosis by a variety of other authors such as Hunter\textsuperscript{12} that a
pressure gradient does not exist in an open capillary solution.

When examining the time independent/static (DC) case of Eq. (1) it is seen that
the viscous forces must equal the electric field forces. Now in the frequency dependent
case, inertial forces must be included in the solution. This can be seen in Eq. (8) where
the second and third terms are the same as in the DC case except that now the terms are
time-varying due to the time varying forcing function in the third term. This time varying
function provides a non-zero term for the first term of Eq. (8). Whereas, in the DC case
where \( \omega \) equals zero, the derivative with respect to time vanishes for the first term of Eq.
(8). In the AC case the first term is differentiable and remains as the inertial term. Upon
examination of Eq. (8), it is obvious that it does not have an exact analytical solution
because there is one equation and two unknowns. To find a solution for this equation, it
was solved using two different regions within the capillary, one near the wall and the
other in the bulk fluid. In order for this solution to be valid, certain restrictions are
required.

The main restriction of this solution is that the viscous skin depth\textsuperscript{9,14},

\[
\delta = \sqrt{\frac{\eta}{\rho \omega}}
\]  


(12)
cannot approach within three Debye lengths of the wall. The viscous skin depth is the
distance away from the no-flow boundary condition at the wall to where the vorticity

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wave has been attenuated by a factor of 2.718 (e). The solution to Eq. (10) is restricted to frequencies less then 1 MHz and to solutions with concentrations greater than $10^{-4}$ M. These restrictions ensure that there are no inertial effects within three Debye lengths of the wall. As part of this solution, it is assumed that the capillary is sufficiently long that end effects can be neglected.

A. Near-Wall Solution

The near-wall solution is for the region where there is a no flow condition at the wall to three Debye lengths away from the wall. Within this region the radius of curvature is negligible, therefore the geometry of the capillary is not included for this portion of the solution. At three Debye lengths from the wall the flow velocity has reached its maximum within this region. As stated earlier in the discussion concerning the restrictions to the solution, there cannot be any inertial effects in the near-wall solution. Therefore, the frequency-dependent electro-osmosis governing equation (10), for the near-wall solution becomes

$$\eta \frac{\partial^2 v_{ew}(x,\omega)}{\partial x^2} = \varepsilon \frac{\partial^2 \phi(x)}{\partial x^2} E(\omega),$$

(13)

where $v_{ew}$ is the electro-osmotic fluid velocity near the wall. The solution of Eq. (13) is

$$v_{ew}(x,\omega) = \frac{\varepsilon \kappa}{\eta} \left[ \exp(-\kappa x) - 1 \right] E(\omega),$$

(14)

which is nearly identical to the DC case except for the frequency component. When examining Eq. (14) it can be seen that the velocity near the wall is always in phase with the driving electric field.
B. **Bulk-Fluid Solution**

Remembering the earlier restrictions on the solution, it was determined that inertial effects are present in the bulk-fluid solution. Consequently, we are left with the original frequency-dependent electro-osmosis equation, Eq. (10) re-shown below for a generalized coordinate system.

\[ i\rho \omega v(r, \omega) = \eta \nabla^2 v(r, \omega) - \varepsilon \nabla^2 \varphi(r) E(\omega) \]  
(15)

where \( r \) is the radial coordinate and \( \nabla^2 \) is the generalized Laplacian operator.

Because we are dealing with the bulk-fluid portion of the solution, the curvature of the capillary must now be taken into account. Also, a different set of boundary conditions exists in the bulk fluid then exists for the near wall solution. In the bulk fluid the potential distribution \( \varphi(r) \) drops to essentially zero, it can also be concluded that in the bulk fluid of the capillary

\[ \nabla^2 \varphi(r) \to 0 \]  
(16)

Consequently, in the bulk-fluid, Eq. (15) becomes,

\[ i\rho \omega v_{eb}(r, \omega) = \eta \nabla^2 v_{eb}(r, \omega). \]  
(17)

Where \( v_{eb} \) represents the electro-osmotic fluid velocity in the bulk fluid. Rearranging Eq. (17) and now using cylindrical coordinates for the capillary geometry with \( r \) being the radial distance from the surface, Eq. (17) takes the form

\[ \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + k^2 \right) v_{eb}(r, \omega) = 0, \]  
(18)
where

\[ k = \sqrt{-\frac{i \rho \omega}{\eta}}. \]  \hspace{1cm} (19)

The general solution to Eq. (16) has the form\(^{15}\)

\[ v(r, \omega) = C_1 J_0(kr) + C_2 Y_0(kr), \]  \hspace{1cm} (20)

where \(J_0\) is a Bessel function of the 1\(^{st}\) kind of order 0 and \(Y_0\) is a Weber's Bessel function of the 2\(^{nd}\) kind of order 0. Noting that \(Y_0(0) = \infty\) requires that \(C_2 = 0\), gives

\[ v(r, \omega) = C_1 J_0(kr), \]  \hspace{1cm} (21)

The boundary conditions of the bulk-fluid solution also requires that at three Debye lengths from the wall the velocity is at its maximum \((v_{em})\) and does not change with frequency. Applying the boundary condition that at \(3/\kappa\) from the wall the velocity is \(v_{em}(\omega)\), \(C_1\) is determined to be

\[ C_1 = \frac{v_{em}(\omega)}{J_0(3\kappa b)}, \]  \hspace{1cm} (22)

where "b" is \(3/\kappa\). Substituting \(C_1\) into Eq. (19) and remembering that at distances from the wall greater than \(3/\kappa\), \(v_{em}(\omega) = -(\zeta/\eta)E(\omega)\), the particular solution becomes

\[ v_{eb}(r, \omega) = -\frac{\varepsilon \zeta E(\omega)}{\eta} \frac{J_0(kr)}{J_0(3\kappa b)} \]  \hspace{1cm} (23)

The bulk fluid electro-osmosis fluid velocity behavior as a function of frequency and radial position in the capillary can be seen in Fig. 4. At low frequencies the velocity
with respect to radial position is constant, and as the frequency increases, the velocity in
the center of the capillary decreases. This is the expected behavior due to inertial effects
in the fluid. To see the complete velocity profile, the near wall and bulk solutions can be
combined to give the approximate combined solution

\[ v_{eb}(r, \omega) = \frac{\varepsilon \zeta E(\omega)}{\eta} \left[ \exp(-kr) \frac{J_0(kr)}{J_0(kb)} \right] \]  

(24)

Equation 24 is plotted in Fig. 5, where it can be seen that the near wall portion of the
velocity profile does not change with frequency.

Because the near wall portion of Eq. (24) does not contribute to the volume flow
the mean velocity determination is made using \( v_{eb}(r, \omega) \), from Eq. (23). This is
accomplished by integrating \( v_{eb}(r, \omega) \) over the section of the capillary and dividing by the
cross-sectional area of the capillary, we have the mean velocity of the fluid in the
capillary, given as

\[ v(\omega) = \frac{1}{\pi a^2} \int_0^a 2\pi r v_{eb}(r, \omega) r dr = \frac{\varepsilon \zeta E(\omega)}{\eta} \frac{2}{ka} \frac{J_1(ka)}{J_0(kb)} \]  

(25)

where “a” is the radius of the capillary. Dividing the mean velocity of the fluid in the
capillary by the electric field, \( E(\omega) \), we have the mobility for frequency-dependent
electro-osmosis in an open capillary given as

\[ u(\omega) = \frac{v(\omega)}{E(\omega)} = \frac{\varepsilon \zeta}{\eta} \frac{2}{ka} \frac{J_1(ka)}{J_0(kb)} = \frac{2u_{de}}{ka} \frac{J_1(ka)}{J_0(kb)} \]  

(26)
where \( u_{dc} \) is the mobility for the DC electro-osmosis case. A plot of the frequency-dependent mobility can be seen in Fig. 6, where the real and imaginary portions of the response are shown for two different capillary sizes. The real part of Eq. (26) has a constant coupling coefficient until the critical frequency is reached, at which time the coupling coefficient starts to decrease with increasing frequency. The imaginary response shows that at low frequencies, virtually no inertial terms are present, and as the frequency is increased, the inertial terms eventually equal the viscous (real) terms. It can also be seen by using the two different capillaries with radii of 100 \( \mu \text{m} \) and 500 \( \mu \text{m} \) that the critical frequency is dependent on the radius of the capillary.

To examine the frequency-dependent behavior of the electro-osmosis coupling coefficient, the volume fluid flow must be determined. This is straightforward, and is achieved by integrating the fluid velocity in Eq. (23) over the cross section of the capillary,

\[
Q_e(\omega) = -2\pi \int_0^a r v_{eB}(r, \omega) dr
\]

(27)
giving

\[
Q_e(\omega) = -2\pi \mathcal{E}(\omega) \frac{e^\zeta}{\eta} a J_1(ka) \frac{J_0(kb)}{k J_0(kb)}
\]

(28)

where \( Q_e \) represents the electro-osmosis volume flow. Eq. (23) is used in the integration for simplicity since the exponential term in Eq. (24) does not contribute to the solution as discussed previously.
C. **Counter-Flow Solution**

As shown in Fig. 2b, if the capillary is closed at both ends, a counter-flow must exist. This counter-flow is driven by the pressure that builds up at the ends of the capillary and the equation describing this situation can be expressed as

\[
i \rho \omega v_c(r, \omega) = \eta \nabla^2 v_c(r, \omega) - \nabla^2 P(\omega)
\]

where \(v_c\) represents the counter-flow velocity and \(P\) is the driving pressure. Eq. (29) indicates that the pressure forces are equal to the viscous forces minus the inertial forces. Eq. (27) has been solved numerous times in prior literature\(^8,^{16,17}\), with the solution given as

\[
v_c(r, \omega) = \frac{\Delta P(\omega)}{n/k^2} \left[ \frac{J_0(kr)}{J_0(ka)} - 1 \right]
\]

where \(l\) is the length of the capillary and \(k\) is the same as defined in Eq. (19). The volume flow is found by integrating counter-flow velocity over the area of the capillary as shown by

\[
Q_c(\omega) = -2\pi \int_0^a rv_c(r, \omega)r \, dr
\]

giving

\[
Q_c(\omega) = \pi a^2 \frac{\Delta P(\omega)}{n/k^2} \left[ \frac{2}{ka} \frac{I_1(ka)}{J_0(ka)} - 1 \right]
\]

where \(Q_c\) is the volume flow through the capillary due to the counter-pressure.
D. Coupling Coefficient Solution

As in the DC case, the coupling coefficient is the ratio of the voltage applied across the sample to the pressure measured across the sample \( \Delta V / \Delta P_m \). Setting \( Q_e \), Eq. (28) equal to \( Q_e \), Eq. (32), and taking the ratio \( \Delta V / \Delta P_m \),

\[
\frac{\Delta V(\omega)}{\Delta P(\omega)} = \frac{a}{2 \epsilon \xi k} \left( \frac{2}{ka} \frac{J_1(ka)}{J_0(ka)} - 1 \right) \left( \frac{J_1(ka)}{J_0(kb)} \right),
\]

which is the AC electro-osmosis coupling coefficient in a closed capillary. It should be noted that \( \Delta E \) has been replaced by \( \Delta V / l \) and the lengths divide out.

Graphically the real and imaginary response of the AC electro-osmosis coupling coefficient for a closed capillary can be seen in Fig. 7. It can be seen that the frequency response has a form similar to the frequency response for the frequency-dependent mobility (Fig. 6) where the real part of Eq. (33) has a constant coupling coefficient until the critical frequency is reached, at which time the coupling coefficient starts to decrease with increasing frequency. The imaginary response shows that at low frequencies, virtually no inertial terms are present, and as the frequency is increased, the inertial terms eventually equal the viscous (real) terms. This corresponds to the coupling coefficient having a maximum phase response of 45 degrees, as shown in Fig. 8. It can also be seen in Fig. 7 that the critical frequency is dependent on the radius of the capillary. This can be seen when plotting the response for two capillaries, one with a diameter of 100 \( \mu m \) and the other with a diameter of 500 \( \mu m \). When FDM and the FDE frequency responses
are compared using a 100 µm diameter capillary, as seen in Fig. 9, the responses are not identical. In fact the electro-osmosis coupling coefficient response has a higher rollover frequency than does the frequency-dependent mobility. It can also be seen in Fig. 10, which shows the frequency responses if Fig. 9 normalized to where inertial effects start to appear in the capillary, that more than the rollover frequency is different between the two responses.

To understand better the frequency response of the frequency-dependent mobility and frequency-dependent electro-osmosis coupling coefficient it is instructive to compare them both to the frequency-dependent streaming potential (FDSP) phenomena since FDSP has been more extensively studied. This is instructive because all three phenomena are based on inertial effects in the center of the capillary retarding fluid motion in the center of the capillary as the frequency is increased. To appreciate the usefulness of this comparison the reader should have a basic understanding of frequency-dependent streaming potentials. The theoretical frequency-dependent streaming potential coupling coefficient is given as

\[
C(\omega) = \frac{\Delta V_{SP}(\omega)}{\Delta P_{SP}(\omega)} = \frac{\varepsilon \zeta}{\sigma \eta} \left[ \frac{2}{ka} \frac{J_1(ka)}{J_0(ka)} \right] = -SP_{dc} \left[ \frac{2}{ka} \frac{J_1(ka)}{J_0(ka)} \right],
\]  

(34)

where \(C(\omega)\) is the frequency-dependent streaming potential coupling coefficient which is the ratio of the voltage (\(\Delta V_{SP}\)) measured across the sample to the differential pressure (\(\Delta P_{SP}\)) applied across the sample and \(\sigma\) is the conductivity of the fluid. The remaining parameters in the Eq. (34) are the same as defined earlier in the paper. It should also be noted that \(\varepsilon \zeta/\sigma \eta\) is the DC streaming potential response. The theoretical frequency-
dependent streaming potential coupling coefficient, Eq. (34), is obtained by calculating the convection current

\[ I_{\text{conv}}(r) = \int v_z(r) \rho_c(r) \, dr \quad , \quad (35) \]

where \( v_z(r) \) is the fluid velocity as given in Eq. (26) and \( \rho_c(r) \) is the charge density as shown in Fig. 1. The convection current occurs when ions near the surface as shown in Fig. 1 are pulled along due to viscous effects in the fluid as the fluid moves tangentially to the surface. This is related to the electro-osmosis case where the ions, which are being moved by an applied electric field, pull the fluid along due to viscous effects in the fluid. In the streaming potential case, the convection current must be balanced by a conduction current to satisfy steady state equilibrium considerations\textsuperscript{18,19}. This is also similar to frequency dependent electro-osmosis where the two volume flows must balance to satisfy steady-state equilibrium conditions. The streaming potential conduction current is determined using Ohm's law where the conductance of the sample is multiplied by the voltage measured across the sample, as shown in Eq. (36).

\[ I_{\text{cond}}(r) = \frac{\pi \sigma a^2}{l} \Delta V \quad (36) \]

The streaming potential coupling coefficient is then determined by setting the convection current equal to the conduction current, then the ratio \( \Delta V/\Delta P \) is taken to determine coupling coefficient as shown in Eq. (34).
A graphical comparison of the frequency-dependent mobility (FDM) frequency-dependent electro-osmosis (FDE) and frequency-dependent streaming potential (FDSP) cases was made and the two responses are identical. The normalized frequency response for FDM and FDSP are identical, but the rollover frequency of the FDE case is higher, Fig. 9. The identical nature of the FDM and FDSP response in further confirmed when comparing the governing equations, Eq. (26) and Eq. (34) respectively. In this comparison the equations are identical except for the constant (σ), which represents the fluid conductivity in the FDSP case. While the FDSP and FDM responses are identical, it is also apparent that the rollover frequency for the FDE response is a little more than three times higher in frequency than that for the FDM and FDSP response. This difference in rollover frequency is due to the hydrodynamics and the viscous skin depth properties.

To understand some of the differences and similarities between the FDM, FDE, and FDSP frequency responses it is instructive to look at the high frequency response for each of the phenomena while revisiting the physics that is driving the phenomena. Examination of the low frequency response does not provide any additional insight since it shows that the frequency response as \( \omega \to 0 \) is the DC limit. Using the high frequency approximations for the Bessel functions in the FDM, FDE, and FDSP solutions, comparisons of the three different high frequency responses can be made.

First we will discuss the FDM and FDSP cases since their frequency response are identical as seen in Eq. (26) and Eq. (34), where the only difference is the DC term which
is constant. High frequency Bessel function approximations can be used when $ka >> 10$, as described by Crandall\textsuperscript{16}. The high-frequency approximation used for the Bessel functions $J_0$ and $J_1$ is given by

$$
\frac{J_1(x \sqrt{-i})}{J_0(x \sqrt{-i})} = -i \quad ,
$$

(37)

which can be found in Crandall\textsuperscript{16} or which can be easily proven using the asymptotic approximations of Abramowitz and Stegun\textsuperscript{20}. In Eq. [26],

$$
ka = a \sqrt[\frac{ip\omega}{\eta}}
$$

(38)

from which the following rearrangement is made to Eq. (38):

$$
x \sqrt{-i} = a \sqrt[\frac{ip\omega}{\eta}] = a \sqrt[\frac{\rho\omega}{\eta}] \sqrt{-i} 
$$

(39)

Then substituting Eq. (39) into Eq. (26) gives

$$
C(\omega)_{ka>10} = \frac{\hat{a}a}{\zeta} \frac{\sqrt{-2i}}{\sqrt{ka}} = \frac{\hat{a}a}{\zeta} \frac{-2i}{\sqrt{-i\nu\rho}}
$$

(40)

Eq. (40) can then be modified to

$$
C(\omega)_{ka>10} = \frac{\varepsilon_\zeta}{\eta} \left[ \frac{-2}{a} \sqrt{\frac{\eta}{\omega\rho}} \left( \frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} \right) \right]
$$

(41)
It has been previously shown\(^8\), that the solution using Bessel function approximations in
the FDSP case is nearly identical to the complete Bessel function solution. The high and
low frequency approximations are identical with a slight divergence in the intermediate
frequency range, \(1 > ka > 10\), which was not accounted for in the approximations.
However, within this region, the error is smaller than measurements can detect.

The significance of Eq. (41) can fully be appreciated when comparing it to the
frequency-dependent hydraulic (FDH) high frequency approximation as done by Reppert
et al.\(^8\), where the hydraulics are the driving force behind FDSP. The FDH transfer
function describing the mean fluid velocity divided by the pressure measured across the
capillary is given by

\[
H(\omega) = \frac{1}{i\omega} + \frac{a\delta}{2\eta}(1 - i) = \frac{1}{i\omega} + \frac{a}{2\eta}\sqrt{\frac{2\eta}{\rho\omega}}(1 - i). \quad (42)
\]

The bulk fluid response is dominated by the inertial affects in the first term.
However, when frequencies are high the viscous skin depth starts to approach the wall.
At this point a second order effect given by the second term in Eq. (42) starts to
dominate. This second order effect shows that in the region near the wall the inertial
terms are equal to the viscous terms. When we compare Eq. (42) to Eq. (41), we see that
the second order effect in the FDH case appears to dominate the whole FDSP high
frequency solution. This comes about do to the integration of the fluid velocity and the
charge density as shown in Eq. (35). The charge density is only of consequence in the
vicinity of the wall and thus the bulk fluid response has little influence on the amount of
charge moved. The bulk fluid however, does play an important role in the pressure gradient and the volume fluid flow.

As demonstrated earlier there is a similarity between the FDM and FDSP solutions given in Eqs. (26 & 34). Understanding the physics of FDSP then gives insight into the physics controlling the FDM solution. It can be concluded that electro-osmotic fluid motion is controlled by the near wall interaction of the electric field with the ions in a viscous fluid. Another way of saying this is that the coupling between the electric field and the fluid in only in the near wall region, which is the expected conclusion for electro-osmosis.

For the FDE high frequency Bessel function approximation, we start with Eq. (33) and rearrange it as

$$\frac{\Delta V(\omega)}{\Delta P(\omega)} = \frac{a^2}{8\varepsilon \xi} \left[ \frac{4}{ka} \left( \frac{2 J_1(ka)}{ka J_0(ka)} - 1 \right) \right], \quad (43)$$

which is a transfer function multiplied by the DC response. Applying the identity of Eq. (37) to Eq. (43) we get

$$\frac{\Delta V(\omega)}{\Delta P(\omega)} = \frac{a^2}{8\varepsilon \xi} \left( \frac{8}{k^2a^2} - \frac{4i}{ka} \right) = \frac{a^2}{8\varepsilon \xi} \left( \frac{8\eta i}{a^2 \rho \omega} - \frac{4}{a} \sqrt{\frac{i\eta}{\rho \omega}} \right), \quad (44)$$

$$\frac{\Delta V(\omega)}{\Delta P(\omega)} = \frac{a^2}{8\varepsilon \xi} \left[ \frac{8\eta i}{a^2 \rho \omega} - \frac{4}{a} \sqrt{\frac{2\eta}{\rho \omega}}(1 + i) \right]. \quad (45)$$
In the FDSP, FDM and FDE cases the very high frequency response falls off as $\omega^{-1/2}$. The FDE case has another effect that contributes to the falloff as $\omega^{-1}$. This effect contributes to the low frequency portion of the high frequency solution. The FDE transform function is caused by the superposition of the electro-osmosis velocity profile and the counter-flow velocity profiles of Fig 11a.

However, this does not adequately explain why the rollover frequency for FDE is higher than the rollover frequency for FDSP and FDM. The rollover frequency for the FDSP, FDM and FDE cases, is controlled by the viscous skin depth, through the term

$$k = \sqrt{-\frac{i\omega}{\eta}} = \frac{\sqrt{-i}}{\delta},$$

(46)

where $\delta$ is the viscous skin depth as defined in Eq.(12). In the FDSP and FDM cases, the viscosity wave emanates from the wall where the fluid velocity goes to zero.

In the FDE case there are two viscosity waves that superpose on each other to give a resultant wave, this resultant wave describes the velocity profiles shown in Fig. 11b and Fig. 12. A viscosity wave is a transverse wave that occurs in a fluid due to the viscosity of the fluid\textsuperscript{14,16}. To describe a viscosity wave, the example of an oscillating plate in a viscous fluid will be used where the plate has infinite length in the y-z direction and the fluid extends infinitely away from the plate in the x direction. As the plate is oscillated in the y-direction, the fluid is moved near the plate due to viscous forces. Due to these viscous forces a transverse wave propagates into the bulk fluid with its velocity perpendicular to the direction of propagation. These transverse waves are rapidly
damped as they move away from the plate. The velocity of these waves, as given by Crandal\textsuperscript{16} and Landau\textsuperscript{14}, is

\[ vel = u_0 \exp\left(-x \sqrt{\frac{\rho \omega}{\eta}}\right) \exp\left(i x \sqrt{\frac{\rho \omega}{\eta}} - \omega t\right), \tag{47} \]

where the first exponential term represents the damping of the wave. As defined earlier the viscous skin depth is when the wave has been damped by a value of $e$. There is duality to the situation just describe. If instead we consider the plate to be stationary and the fluid to be moving with laminar flow, the same transverse wave will emanate from the plate.

As we apply this to a capillary the wavelength of the wave is much longer than the diameter of the capillary for the capillary sizes and frequencies we are considering. For FDE there is a transverse wave emanating from the walls of the capillary in the shape of plug flow as shown in Fig. 11a. There is also a transverse wave, 180 degrees out of phase, emanating from the wall caused by the counter flow, also shown in Fig 11a. Figure 11b shows the superposition of these two waves. As can be seen this resultant wave has nodes (zero velocity points) at the walls and at a distance "r" from the walls. This node at a distance "r" from the wall acts as a tie down point just as the nodes at the walls act as tie down points. Therefore, these nodes in the interior of the capillary can be thought of as the starting point for an entirely new wave that is emanating from the interior velocity zero position. This new wave will have an attenuation curve derived
from the interior velocity zero. Consequently, this interior node acts to effectively decrease the radius of the capillary.

This situation can be visualized when looking at Fig. 12 where the frequency-dependent electro-osmosis velocity profile for a closed capillary is shown from the wall to the center of the capillary for two capillaries of different diameter. For both capillaries the effective radius of the capillary is reduced. To understand this problem it is also useful to look at the velocity profile in the frequency-velocity-distance space as shown in Fig. 13 where the fluid velocity profiles for a 0.127 mm diameter capillary is plotted from zero to one thousand hertz. It becomes quite evident in this figure how inertial effects are damping out the fluid velocity (or shall we say the transverse wave) in the center of the capillary at high frequencies. It is also seen the near the wall, inertial effects do not impact the fluid velocity.

To verify that the internal velocity zero is acting as a new effective radius for the capillary, a simplified test is used. As discussed earlier, the FDM and FDSP frequency responses are identical and are based on the viscosity wave emanating from the wall. The new effective radius determined from the interior velocity zeros will by substituted for the actual radius in the FDM coupling coefficient equation. The frequency at which inertial effects start to appear in the numeric solution is then compared to the FDE solution where the true radius was used in the solution. It is found that inertial effects started to appear at 16 Hz for both numeric solutions. This approach was chosen because the transfer function for the two solutions are different and the final solutions cannot be
compared. However, the low frequency portion of the solutions are identical and the frequency that inertial effects start to become evident should not depend on the falloff of the curve with frequency, but rather only on the radius or effective radius of the capillary. A comparison of the two curves can be seen in Fig. 14. At low frequencies both curves are controlled by the DC response. At very high frequencies, both curves falloff as $\omega^{-1/2}$. The difference in the transfer functions is evident in the intermediate frequency range.

IV. Experimental Results

Data were collected on a 0.127 mm glass capillary in a pseudo-closed system, where one end of the capillary was closed and the other end was attached to an infinite reservoir. The pressure was monitored using a Brüel & Kjaer miniature hydrophone, model 8103, which has a voltage sensitivity of 26.7 $\mu$V/Pa. The voltage and pressure were monitored using a Labview® 12 bit AD board, and the signals were processed using Fourier analysis. The solution chemistry was 0.001 M KCl and had been allowed to achieve equilibrium with the capillary for a period of two weeks.

Fig. 15 shows the frequency-dependent electro-osmosis magnitude data collected using a 0.127 mm capillary. Plotted along with the data is the theoretical magnitude curve for a 0.127 mm capillary that was generated using the equation for the frequency-dependent electro-osmosis coupling coefficient, Eq. (33). Fig. 15 shows that there is excellent agreement between the theory and the data.
V. Conclusion

The theory for frequency-dependent electro-osmosis in a closed capillary has been presented, showing that the frequency-dependent behavior is a function of the capillary diameter. It has also been shown that frequency-dependent electro-osmosis in a closed capillary changes the effective radius of the capillary. This is due to the superposition of the viscosity waves generated by the electro-osmotic flow and the associated counter flow. The theory was compared to data collected using a 0.127 mm capillary and found to be in good agreement. The results of this investigation may implies that frequency-dependent electro-osmosis can be used to determine pore sizes of capillaries and possibly porous media.

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VII. References


Fig. 1 – a) Simplified schematic representation of the electrical double layer where (OH) is the outer Helmholtz or Stern plane, (S) is the slipping plane, and the diffuse zone is represented by a diminished number of ions. b) Simplified schematic representation of the potential distribution in the electrical double layer, where $\varphi_0$ is the potential at the surface, $\varphi_d$ is the potential at the Stern plane, and $\zeta$ is the potential at the slipping plane.
OPEN SYSTEM

CLOSED SYSTEM

Velocity of Electro-osmotic Flow

Flow velocity Due To Counter Pressure

≈3/κ

E Field

a) E Field

b)

1/κ = Debye Length

Fig. 2 – Simplified schematic representation of electro-osmotic flow in open and closed capillaries. In the open capillary, Fig. 2a, the electro-osmotic flow is shown as a plug flow which has its maximum velocity at approximately 3 Debye lengths from the wall. In the closed capillary, Fig. 2b, the electro-osmotic flow must be balanced by a counter flow. The actual fluid velocity is the sum of the electro-osmotic flow and the counter flow.
Fig. 3 – DC electro-osmotic velocity profile in a capillary, from the wall to the center of the capillary. At approximately 3 Debye lengths from the wall the fluid is at its maximum velocity.
Fig. 4 – Bulk fluid frequency-dependent electro-osmotic velocity profile in a capillary.

The plot shows the velocity profiles from 3 Debye lengths away from the wall to the center of the capillary. At low frequencies there are no inertial effects present in the bulk fluid. However as the frequency is increased, the inertial effects become more prevalent in the center of the capillary.
Fig. 5 – Near wall and bulk fluid frequency-dependent electro-osmotic velocity profile in a capillary. The plot shows the velocity profiles from 3 Debye lengths away from the wall to the center of the capillary. At low frequencies there are no inertial effects present in the bulk fluid. However as the frequency is increased, the inertial effects become more prevalent in the center of the capillary. It can also be seen that for all frequencies there are no inertial effects in the near wall region.
Fig. 6 – Normalized frequency-dependent mobility in a capillary, with real and imaginary portions of the response shown for a 100 μm and 500 μm diameter capillary.
Fig. 7 - Normalized frequency-dependent electro-osmosis in a closed capillary, with real and imaginary portions of the response shown for a 100 µm and 500 µm diameter capillary. The response for the 100 µm capillary as a higher rollover frequency than does the 500 µm capillary.
Fig. 8 – The electro-osmosis frequency-dependent coupling coefficient phase response is shown for a 100 µm and 500 µm diameter capillary. As 45 degrees is approached at the high frequencies, the phase is in agreement with the real and imaginary portions of the coupling coefficient which are approaching equality equal in magnitude.
Fig. 9- Comparison of normalized FDE and FDM responses for a 100 µm and 500 µm capillary. It is seen that the FDE response has a higher rollover frequency than does the FDM response.
Fig. 10 – Comparison of normalized FDE and FDM responses for a 100 μm diameter capillary. The response has also been normalized such that the inertial effects start to occur at the same frequency. It is apparent the frequency responses are still different.
Fig. 11 — a) Schematic diagram representing the velocity profile for streaming potential Poiseuille flow and plug flow. The Poiseuille flow is associated with FDSP and the counter flow in FDE. The plug flow is associated with FDM and the driving flow in FDE. b) Schematic diagram representing electro-osmosis flow in a closed capillary. It can be seen in these diagrams that the electro-osmosis velocity profile has two zeros, one at the wall and one at a distance from the wall, while the Poiseuille velocity profile has one zero at the wall. The electro-osmosis diagram is not to scale, the $3/\kappa$ line is shown to represent an approximate distance.
Fig. 12 – FDE velocity profile for a 100 μm and a 500 μm diameter capillary. It can be seen that the second velocity zero does shift with capillary size.
Fig. 13 – Velocity profile for FDE in three dimensions. It can be seen that at high frequencies the fluid motion has experienced attenuation in the center of the capillary while along the walls to attenuation is apparent.
Fig. 14 — Normalized plot of FDM and FDE in a 0.127 mm diameter capillary, where the FDM plot has been made using a capillary whose effective radius has been reduced by the distance from the wall to the second velocity zero. For both plots inertial effects start at 16 Hz.
Fig. 15 – Comparison of magnitude frequency-dependent electro-osmosis coupling coefficient data collected on a 0.127 mm diameter capillary with the theoretical magnitude curve for the same size capillary. There is excellent agreement between the data and the theory. The capillary had 0.001 M KCL solution as the electrolyte.