Electrokinetics in the Earth

By

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Abstract

The study of Streaming potentials has applications in the earth sciences, ranging from fluid flow monitoring, to permeability determination, to studying the surface chemistry of rocks and minerals. In this thesis study of frequency-dependent electrokinetics is presented with both theoretical development and experimental verification. The complex (real and imaginary) streaming potential coupling coefficient is explained. This is followed by the first experiments to measure the real and imaginary part of frequency-dependent streaming potential coupling coefficients. As part of this study an experimental apparatus and data acquisition system were constructed to measure the streaming potential coupling coefficients as a function of frequency. The purpose of the experiments was to measure, for the first time, the real and imaginary part of streaming potentials. In addition, the measured frequency range was extended beyond any previous measurements. Frequency-dependent streaming potential experiments were conducted on one glass capillary, two porous glass filters, and one rock. The sample pore diameters ranged from 34 micrometers to 1 millimeter. Without these experiments, the validity of modeling of the frequency dependence of the seismorelectric effect using existing models streaming potential models would be in question. Two frequency-dependent models (Packard and Pride) were compared to the data. Both Pride’s and Packard’s models have a good fit to the experimental data in the low and intermediate frequency regime where viscous terms dominate in the fluid. In the high frequency regime, where inertial terms start to dominate, the data fits the theory after being corrected for capacitance effects of the experimental setup. Pride’s generalized model appears to have the ability to more accurately estimate pore sizes in the porous medium samples. Packard’s model has one unknown model parameter whereas Pride’s model has four unknown model parameters, two of which can be independently determined experimentally. Pride’s additional parameters may allow for a determination of permeability.

As part of the study of frequency-dependent electrokinetics, this thesis presents the theory for frequency-dependent electroosmosis. It is shown that the electroosmosis frequency-dependent coupling coefficient is constant with increasing frequency until the critical frequency is reached, at which point the coupling coefficient starts to decrease
with increasing frequency. The frequency response of the electroosmosis coupling coefficient is dependent on the capillary radius. The smaller the capillary radius the higher the critical frequency. Data is presented for a 0.127 mm capillary.

In addition to studying frequency-dependent electrokinetics, this thesis examines the temperature-dependent behavior of streaming potential coupling coefficients. As part of this examination a review is made of the previous literature that discusses the temperature dependence of streaming potentials. The streaming potential coupling coefficient is determined using the permittivity, the conductivity, and the viscosity of the fluid. It has been determined that the temperature-dependent behavior of the permittivity, conductivity, and viscosity are well documented and do not alone account for temperature dependence of streaming potentials. The other quantity used in calculating the streaming potential coupling coefficient is the zeta potential. The temperature dependence of the zeta potential is not well understood at the present time. By examining the theory, it appears that the zeta potential temperature dependence is controlled by the fluid concentration and the adsorption properties of the surface.

After examining the theory, streaming potential experiments at elevated temperature and pressure were conducted on Fontainebleau Sandstone, Berea Sandstone, and Westerly Granite. The experiments were conducted in a pressure vessel with temperatures ranging from 23°C to 200°C at pore pressure ranging from 20 bar to 50 bar and confining pressures ranging from 200 bar to 250 bar. The zeta potential was found to increase with increasing temperature, and the coupling coefficient can increase or decrease depending on how the conductivity of the sample varies. This implies that in geothermal regions, streaming potentials can have large magnitudes depending on the conductivity of the geothermal fluid.

Thesis supervisor: F. Dale Morgan
Title: Professor of Geophysics
To my parents

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Whose guidance in my early years has made my studies at MIT possible.
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Chapter 1
Introduction

1.1 Background

Electrokinetics is a broad term that covers the specific areas of streaming potentials, electroosmosis, electrophoresis, and sedimentation potentials. In general, electrokinetics is the study of how a charged surface interacts with an ionic fluid. The field of electrokinetics is often studied to obtain information concerning the surface chemistry at the solid/fluid interface. The study of streaming potentials deals with the voltage that is generated when an ionic fluid moves tangentially to a charged surface. Electroosmosis studies the surface/fluid interfacial properties by looking at the fluid motion that occurs tangentially to a surface when an electric field is applied tangentially
to the surface. Electrophoresis and sedimentation potentials are counterparts of streaming potentials and electroosmosis. Electrophoresis refers to the motion of a particle that is induced tangentially to an applied electric field, whereas sedimentation potentials occur when a particle falls in a liquid and a potential is developed parallel to the falling motion. Specifically, this thesis is primarily concerned with streaming potentials. In addition to the primary focus on streaming potentials, a theory for frequency-dependent electroosmosis is also developed.

Streaming potentials can occur within a variety of materials and are used in fields ranging from medicine [Mestel et al., 1998], the paper industry [Beck et al., 1978], or to any industry where information on the surface charge or the surface/fluid interface is desired. In the field of geophysics, the study of streaming potentials can provide geophysicists with useful information for studying the earth and examining rocks in the laboratory. Since streaming potentials are generated by fluid flow, information about in situ underground hydrogeological fluid flow can be determined by measuring streaming potentials at the surface. Also, Packard in 1952 showed that the frequency response of streaming potentials in capillaries is determined by the diameter of the capillary. In 1994, Pride extended the theory to porous media and showed that a relationship exists between the frequency response and the permeability of the porous medium. It can be seen that streaming potentials have a wide range of possible applications in geophysics, from determining the charge on rock surfaces, to understanding the rock/fluid interfacial chemistry, to monitoring in situ hydrogeological flow.
Electroosmosis, being closely related to streaming potentials, has many of the same applications as streaming potentials. However, there is not widespread use of electroosmosis in geophysics as an investigation tool due to practical considerations. Also, streaming potentials occur naturally whereas in electroosmosis one must supply the driving force in order to use electroosmosis.

1.2 Objective

This thesis has several objectives, with the overall objective to increase our understanding electrokinetic phenomenon in the earth. Specifically, the first part of the thesis is concerned with looking at the frequency-dependent behavior of streaming potentials and electroosmosis. The objective of the first part of this thesis is to do experiments that for the first time measure the real and imaginary components of frequency-dependent streaming potential coupling. The second objective is to develop the first analytical expression to describe the behavior of frequency-dependent electroosmosis coupling coefficients and verify the theory with an experiment. The second part of this thesis is concerned with the effects of temperature on streaming potentials. The objective in this section is to develop a method for measuring streaming potential coupling coefficients for rocks at elevated temperature and pressures that can simulate in situ conditions. While achieving these primary objectives, secondary objectives are also achieved. The secondary objectives are described in the individual chapters of the thesis.
1.3 Thesis Organization

The thesis examines three different aspects of electrokinetics as they may be applied to geophysics. Chapter 2 examines the frequency behavior of streaming potentials. The emphasis of Chapter 2 pertains to the real and imaginary components of frequency-dependent streaming potentials and their physical interpretation. After the physical interpretation of streaming potentials has been explained, a comparison of Packard’s and Pride’s theories is presented. This is followed by the first-ever real and imaginary (complex) frequency-dependent streaming potential coupling coefficient data on capillaries and porous media.

Chapter 3 looks at a second area of electrokinetics: the frequency response of electroosmosis. Prior to the theory presented in this chapter, there was no analytical expression for the frequency-dependent electroosmosis coupling coefficient. Chapter 3 first presents a review of DC electroosmosis followed by the development of the theory for frequency-dependent electroosmosis in a capillary. The theory is then confirmed by experimental data.

Chapter 4 investigates some of the possible applications of frequency-dependent streaming potentials and frequency-dependent electroosmosis. The advantages of the different methods are discussed along with their major limitations. The chapter
concludes by listing some of the future work required to make the methods more practical in the future.

Chapter 5 provides a theory for streaming potentials at elevated temperature and pressure. First, a general review of streaming potentials is made, which is followed by a literature review of streaming potentials at elevated temperature. After the review of previous work on streaming potentials at elevated temperature, the development of the theory of streaming potentials at elevated temperature is presented. The chapter is concluded with a presentation of the temperature dependence of the zeta potential.

Chapter 6 presents the experimental results for streaming potential experiments at elevated temperature and pressure. First the experimental apparatus is described, followed by the development of the experimental methodology. The data on streaming potential and zeta potentials are then presented, followed by a comparison of the data to the model of chapter 5. Lastly, geophysical applications of streaming potentials at elevated temperature and pressure are presented.

Chapter 7 summarizes the results and conclusions of the thesis, which is followed by Appendix A. Appendix A addresses DC, AC, and transient streaming potential data collection and processing techniques. First the DC method is addressed, followed by the AC method and then the transient method.
Chapter 2

Frequency Dependent Streaming Potentials

2.1 Introduction

The phenomenon of streaming potentials has been studied for many years. This has led to applications in such diverse fields as chemistry, biology and geophysics, (Kurtz, Findl and Stormo\textsuperscript{1}, Levine, Marriott, Neale, and Epstein\textsuperscript{2}, Rice and Whitehead\textsuperscript{3}, Morgan, Williams and Madden\textsuperscript{4}, Ishido and Mizutani\textsuperscript{5}). The overwhelming majority of this work has been in the area of DC streaming potentials, while very little work has been done in the area of frequency-dependent streaming potentials. Past theoretical and
experimental work dealing with the frequency response of streaming potentials has dealt
with single-frequency, low-frequency and frequency-response measurements. Single-
frequency streaming potential measurements are made at one frequency while varying the
pressure in order to get plots of streaming potentials versus pressure without using a flow
through apparatus, (Sears and Groves\textsuperscript{6}). Low-frequency measurements are used to
extrapolate the frequency-dependent streaming potential value to the DC limit. This is
done for the purposes of determining the zeta or surface potentials (Pengra et al.\textsuperscript{7},
Wong\textsuperscript{8}). Low-frequency measurements are also used to determine the effective pore size
and hydraulic permeability (Li, Pengra and Wong\textsuperscript{9}). Frequency response measurements
examine the frequency-dependent behavior of streaming potentials (Packard\textsuperscript{10} and
Cooke\textsuperscript{11}). Packard\textsuperscript{10} proposed a frequency-dependent streaming potential theory for
capillaries, where the streaming potential coupling coefficient remains constant at its DC
value until the critical frequency is approached by the sinusoidal driving force. At
frequencies higher than the critical frequency, the streaming potential coupling
coefficient decays with increasing frequency. Packard’s experiments were performed on
a limited number of capillary samples of large radii (2.083 - 0.589 mm) and with no
changes in solution chemistry. Packard was able to achieve a maximum measuring
frequency of 200 Hz. Cooke\textsuperscript{11} attempted to duplicate Packard’s work, but with limited
success; he could not match his capillary data to the theoretical curves of Packard.
Cooke’s data for porous glass filters appears to have the expected trend predicted by
Packard’s theory. On closer examination however, Packard’s theory cannot be
satisfactorily fitted to Cooke’s data. No one to date has satisfactorily fitted frequency-
dependent streaming potential data to theoretical curves for porous media of any pore diameter or for capillaries with diameters less than 155 micrometers.

In 1994, Pride\textsuperscript{12} proposed a generalized theory for frequency-dependent streaming potentials in porous media. This theory relates the transport properties and pore-geometry parameters to the samples streaming potential frequency-response behavior. No experimental work has been performed to validate Pride’s theory.

The understanding of frequency-dependent streaming potentials is vital to Earth scientists who study the electromagnetic signals generated by seismic/acoustic waves propagating in the earth. Earth scientists believe that these electromagnetic signals are generated by oscillatory fluid flow in rocks relative to the mineral matrix\textsuperscript{13}. This relative flow induces a streaming current, which oscillates as an electric dipole at the same frequency as the seismic/acoustic wave exciting the medium. This frequency-dependent streaming current has a counter-current which flows through the conductive part of the rock (bulk fluid) to develop a frequency-dependent streaming potential. Frequency-dependent streaming potentials induced by a seismic wave are often referred to as the seismoelectric effect\textsuperscript{14,15}. Some Earth scientists believe that the streaming-potential frequency response may be useful in determining in-situ permeability\textsuperscript{16,17}.

In this paper, the real and imaginary streaming potential frequency response for a capillary is developed based on Packard’s model, which is then compared to Pride’s model. Then a discussion of the experimental system and methodology is provided. This
is followed by a presentation of the first data where the complex frequency response for one glass capillary and two porous glass filters is presented. These experiments cover a frequency range of 1-500 Hz.

2.2 DC Streaming Potentials

Streaming potentials are a subset of electrokinetic phenomenon, which includes electroosmosis, electrophoresis, and sedimentation potentials. Electrokinetic phenomena are a consequence of a mobile space charge region that exists at the interfacial boundary of two different phases. This region is commonly referred to as the electrical double layer (EDL). The most simplified approximations of the EDL can be represented by a parallel-plate capacitor (Helmholtz model), or a charge distribution that decays exponentially away from the surface (Gouy-Chapman model)\(^{18}\). A more accurate model takes into account the finite size of ions by combining the Helmholtz and Gouy-Chapman models where a fixed layer exists at the surface (Stern layer) and a diffuse layer extends from the fixed layer into the bulk solution (Gouy-Chapman diffuse layer). This model is often referred to as the Stern model of the electrical double layer. More specifically the interfacial region, shown schematically in Figure 2.1, consists of the inner Helmholtz plane (IH) where ions are adsorbed to the surface and an outer Helmholtz plane (OH) where ions are rigidly held by electrostatic forces and cannot move. The closest plane to the surface at which fluid motion can take place is called the slipping plane. The slipping plane has a potential defined as the zeta potential (\(\zeta\)), which is a characteristic of the solid and liquid that constitute the interface. The diffuse layer extends from the OH into the
Figure 2.1 - a) The Stern model of the electrical double layer. b) One of the possible potential distributions of the Stern model. This model assumes that in the Stern layer the potential varies linearly.
bulk of the liquid phase. The distance at which the diffuse layer potential \(\psi_e\) has been reduced to \(\psi_e/\epsilon\) is referred to as the Debye length. This is often used as a measure of how far the diffuse layer extends into the bulk fluid.

Streaming potentials occur when relative motion between the two phases displaces ions tangentially along the slipping plane by viscous effects in the liquid. This displacement of ions generates a convection current \((I_{\text{conv}})\) and has properties similar to an ideal current source. For a capillary, \(I_{\text{conv}}\) is defined by

\[
I_{\text{conv}}(r) = \int v(r)\rho_c(r)dr
\]

(2.1)

in which \(v(r)\) is the fluid particle velocity and \(\rho_c(r)\) is the charge distribution in the capillary. The solution to this integral can be found in a variety of texts and is given by

\[
I_{\text{conv}}(r) = \frac{\pi \epsilon a^2 \zeta \Delta P}{\eta l}
\]

(2.2)

where \(\epsilon\) is the permittivity of the fluid, "\(a\)" is the radius of the capillary, \(l\) is the length of the capillary, \(\Delta P\) is the pressure across the sample, \(\eta\) is the viscosity of the fluid, and \(\zeta\) is the zeta potential.

In steady-state equilibrium the convection current must be balanced by a conduction current \((I_{\text{cond}})\). Hence by ohms law,

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

(2.3)
where $\sigma$ is the fluid conductivity and $\Delta V$ is the voltage measured across the sample. Equating the convection and conduction currents, which must be equal at equilibrium, leads to the Helmholtz-Smoluchowski equation\(^{18}\)

\[
\Delta V = \frac{\varepsilon \zeta}{\eta \sigma} \Delta P^* \tag{2.4}
\]

It should be noted when viewing this equation that it does not include geometry terms for the specimen. The ratio $\Delta V/\Delta P$ will be referred to as the cross-coupling coefficient or simply the coupling coefficient in the rest of the paper. When the capillary or pore-space thickness approach the dimensions of the diffuse layer 0.01 micrometers for 0.001 molar solution) surface effects must be considered\(^{2,4}\). The radii of the samples used in our experiments are much larger than the Debye length; hence these effects will not be addressed.

### 2.3 AC Streaming Potentials

The basic principles of AC streaming potentials will be presented following the methodology of Packard\(^{10}\). To better understand the physics of AC streaming potentials, appropriate comparisons will be made to the frequency-dependent hydraulic problem previously solved by others\(^{19}\).

The basic electrokinetic principles of DC and AC streaming potentials are the same. The difference is in the hydrodynamic part of the solution where the constant pressure of the DC case is replaced by a sinusoidal pressure in the AC case. Therefore,
the starting point for the derivation must go back to the hydrodynamic problem where the Navier-Stokes equation,

$$ \rho \frac{\partial \vec{v}(r, \omega)}{\partial t} \exp(-i\omega t) = -\nabla P(\omega) \exp(-i\omega t) + \eta \nabla^2 \vec{v}(r, \omega) \exp(-i\omega t), \quad (2.5) $$

is shown with a sinusoidal driving pressure applied across the sample. Equation (2.5) can be rearranged into the form

$$ \left[ \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + k^2 \right] \vec{v}(r, \omega) = \frac{\Delta P(\omega)}{\eta l}, \quad (2.6) $$

where the gradient of the pressure has been replaced by $\Delta P(\omega)/l$ and

$$ k^2 = \frac{-i\omega \rho}{\eta}. \quad (2.7) $$

It is apparent that the solution can be expressed using Bessel functions, with the general solution to equation (2.6) expressed as

$$ \vec{v}(r, \omega) = -\frac{\Delta P(\omega)}{k^2 l \eta} + C_1 J_0(kr) + C_2 Y_0(kr). \quad (2.8) $$

The applied boundary conditions are $v(r, \omega) = 0$, when $r = a$; $v(r, \omega) = $ finite, when $r = 0$, and also noting $Y_0(0) = \infty$, which then requires that $C_2 = 0$. This leads to

$$ C_1 = -\frac{\Delta P(\omega)}{\eta/k^2} \frac{1}{J_0(ka)}. \quad (2.9) $$
Substituting equation (2.9) into equation (2.8) gives

\[ \bar{v}(r, \omega) = \frac{\Delta P(\omega)}{\eta kr} \left[ \frac{J_0(kr)}{J_0(ka)} - 1 \right], \quad (2.10) \]

as the frequency dependent velocity inside a capillary. Integrating equation (2.10) over the cross sectional area of the capillary gives

\[ v(\omega) = \frac{\Delta P(\omega)}{\eta kr} \left[ \frac{2}{ka} \frac{J_1(ka)}{J_0(ka)} - 1 \right], \quad (2.11) \]

as the average fluid velocity inside a capillary, which is the frequency-dependent hydraulic solution for a capillary.

Now that the frequency-dependent fluid flow inside a capillary has been presented, equation (2.10) can be substituted into equation (2.1) to give

\[ I_{\text{conv}}(\omega) = \int 2\pi r \rho_c(r) \bar{v}(r, \omega) \, dr, \quad (2.12) \]

which is the frequency-dependent convection current inside a capillary, where the charge density in the capillary in cylindrical coordinates is given by

\[ \rho_c(r) = -\varepsilon \nabla^2 \psi_o(r) = -\frac{\varepsilon}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \psi_o(r)}{\partial r} \right). \quad (2.13) \]

Integrating equation (2.12) from the center of the capillary to the slipping plane under the assumption that the capillary radius is large compared to the Debye length of the EDL\textsuperscript{10,12} gives
\[ I_{\text{conv}}(\omega) = -\frac{2\pi e \alpha \Delta P(\omega) J_1(ka)}{\eta l k J_0(ka)}, \]  

(2.14)

as the frequency-dependent convection current for a capillary.

As in the DC case, at equilibrium, the convection current must be balanced by a conduction current. The conduction current is determined using Ohm's law, where the conduction current is given by

\[ I_{\text{cond}}(\omega) = \Delta V(\omega) \frac{\alpha}{l} a^2 \frac{\sigma}{\eta}. \]  

(2.15)

Setting the convection current equal to the conduction current gives

\[ C(\omega) = \frac{\Delta V(\omega)}{\Delta P(\omega)} = \left[ \frac{\varepsilon \zeta}{\sigma \eta} \right] - 2 \frac{J_1(ka)}{ka J_0(ka)}. \]  

(2.16)

This is the AC Helmholtz-Smoluchowski equation in a form similar to that presented by Packard\textsuperscript{10}, where \( C(\omega) \) is the frequency-dependent cross-coupling coefficient. The AC Helmholtz-Smoluchowski equation reduces to the DC form in the limit as \( \omega \) goes to zero, which can be demonstrated using Bessel function recursive relations or by taking the low-frequency approximation of equation (2.16). Figure 2.2 shows the real and imaginary portions of the AC coupling coefficient, equation (2.16) and a plot of the frequency-dependent hydraulic equation, equation (2.11). Figure 2.3 shows the phase part of equations (2.11) and (2.16). It can be seen in these two figures that the general behavior of the two equations is similar. In particular, the low-frequency behavior is identical but the high-frequency behavior diverges as one goes to higher frequencies.
Figure 2.2 – Comparison of the real and imaginary portions of frequency dependent coupling coefficients and frequency dependent hydraulics.
Figure 2.3 – Phase comparison of the frequency dependent coupling coefficients and frequency dependent hydraulics, where the phase is $0^\circ$ for both curves at 0 Hz.
At first examination of frequency-dependent streaming potentials and frequency-dependent hydraulics, it might be expected that the two phenomena would have identical behavior, since the frequency dependent streaming potential behavior is governed by the frequency-dependent fluid flow. The different responses of the AC Helmholtz-Smoluchowski equation, equation (2.16) and the frequency-dependent hydraulic equation, equation (2.11), are easier to understand by looking at the series and asymptotic approximations for the low and high frequency cases, respectively. Following the methodology of Crandall\textsuperscript{20} (which was developed for the acoustic case), the low-frequency and high-frequency approximations will be made. The two separate equations will then be combined to form a single equation.

Starting with the AC Helmholtz-Smoluchowski expression, equation (2.16) and substituting the low-frequency approximations of the Bessel functions\textsuperscript{20} \( J_0 \) and \( J_1 \), with

\[
J_0(x) = \sum_{n=0}^{\infty} \frac{\left( -\frac{1}{4} x^2 \right)^n}{k! \Gamma(n + 1)} \quad (2.17)
\]

and

\[
J_1(x) = \sum_{n=0}^{\infty} \frac{\left( -\frac{1}{4} x^2 \right)^n}{2^n k! \Gamma(n + 2)} \quad (2.18)
\]
where $x$ represents $ka$ and $ka < 1$. Substituting these two approximations into equation (16) and taking the Lim $n \to \infty$ gives

$$
\frac{\Delta V(\omega)}{\Delta P(\omega)} = \text{Lim}_{n \to \infty} \left[ \frac{\varepsilon \zeta}{\sigma \eta} \left( \frac{2}{ka} \left\{ \frac{x}{2} \sum_{n=0}^{\infty} \frac{(-1/4)^n}{k! \Gamma(n+2)} \right\} \right) \right] = \left[ \frac{\varepsilon \zeta}{\sigma \eta} \right] \left[ \frac{2}{ka} \frac{x}{2} \right] . \tag{2.19}
$$

Since $x = ka$, the low frequency approximation reduces to

$$
C_{\text{ka-cl}}(\omega) = \frac{\Delta V(\omega)}{\Delta P(\omega)} = \left[ \frac{\varepsilon \zeta}{\sigma \eta} \right] = \frac{\Delta V}{\Delta P} . \tag{2.20}
$$

The high-frequency approximation used for the Bessel functions $J_0$ and $J_1$ are given by

$$
\frac{J_1(x \sqrt{-i})}{J_0(x \sqrt{-i})} = -i , \tag{2.21}
$$

which can be found in Crandall\textsuperscript{18} or which can be easily proven using the asymptotic approximations of Abramowitz and Stegun\textsuperscript{21}. In equation (2.16),

$$
ka = a \sqrt{\frac{i \rho \omega}{\eta}} \tag{2.22}
$$

from which the following substitution is made in equation (2.22):

$$
x \sqrt{-i} = a \sqrt{\frac{i \rho \omega}{\eta}} = a \sqrt{\rho \omega \sqrt{-i}} . \tag{2.23}
$$
Then substituting equation (2.21) into equation (2.16) gives

\[
C(\omega)_{ka>10} = \left[ \frac{\varepsilon_\xi}{\sigma \eta} \right] \left[ \frac{-2i}{ka} \right] = \left[ \frac{\varepsilon_\xi}{\sigma \eta} \right] \left[ \frac{-2i}{a \sqrt{-i \omega \eta}} \right] .
\]  

(2.24)

Equation (1.24) can then be modified to

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

(2.25)

Combining the low-frequency and high-frequency approximations gives

\[
CA(\omega) = \left[ \frac{\varepsilon_\xi}{\sigma \eta} \right] \left[ 1 - \frac{2}{a} \sqrt{\frac{\eta}{\omega \rho}} \left( \frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}}i \right) \right] ,
\]  

(2.26)

where \( CA(\omega) \) represents the approximated cross-coupling coefficient. In Figure 2.4, the solution using Bessel function approximations, equation (2.26) is plotted against the Bessel function solution of equation (2.16). It can be seen in Figure 2.4 that the two solutions are nearly identical. There is a slight divergence in the intermediate frequency range, \( 1 > ka > 10 \), which was not accounted for in the approximation. However, the error is smaller than measurements can detect.

It can be seen in equation (2.26) and Figures 2.2, 2.3, and 2.4 that as the frequency is increased, inertial effects start to retard the motion of the fluid within the pore space. This occurs as the fluid makes a transition from viscous dominated flow to
Figure 2.4 – Comparison of the Bessel function solution, solid line, equation (16), to the approximated Bessel function solution open circles, equation (26).
inertial dominated flow. At the higher frequencies the flow becomes inefficient, requiring more energy to move the same amount of liquid the same distance. Therefore at frequencies higher than the transition from viscous to inertial flow, more pressure is required to shear the same quantity of ions from the diffuse zone than when strictly in the viscous flow regime. It can also be seen in equation (2.26) and Figure 2.4 that at higher frequencies the real and imaginary parts of the solution are decreasing at the same rate. This explains the 45 degree phase angle found at high frequencies in Figure 2.3.

One might ask why frequency dependent-hydraulics and frequency-dependent streaming potentials do not have the same behavior. By comparing the form of the frequency-dependent streaming potential (FSP) approximate solution to the frequency-dependent hydraulic (FDH) solution, valuable insight into the physics that causes the difference in behavior between FDH and FSP solutions can be obtained. This comparison will be made using equations (2.20, 2.25, 2.26), of the FDP approximation to the approximation of the (FDH) solution, equation (2.11). The low-frequency approximation to equation (2.11) is

$$H(\omega) = \left( \frac{8}{a^2} + \frac{4 - i\rho\omega}{3} \right)^{-1},$$  \hspace{1cm} (2.27)

where $H(\omega)$ represents the frequency-dependent hydraulic solution. When $ka < 1$, the real term in equation (2.27) dominates over the imaginary term. This implies that at low frequencies the flow is real and as the frequency is increased, an inertial component starts to develop in the flow. However, when $ka < 1$ the inertial term remains insignificant and
the flow is essentially viscous. Therefore, both low-frequency FDH and FSP solution approximations approach the DC limit at low frequencies.

The high-frequency approximation of the FDH equation is given by

$$H(\omega) = \left(\frac{i\rho}{k_a} + \frac{1}{r} \sqrt{\frac{\rho \omega}{2\eta}} (1 + i)\right)^{-1}, \quad (2.28)$$

where $(2\eta/\rho\omega)^{1/2}$ is the viscous skin depth. When examining equation (2.28), it can be seen that the bulk of the fluid is governed by the imaginary terms and thus inertial flow exists. However, when the viscous skin depth is sufficiently small, a second-order effect starts to dominate and the imaginary term starts to decrease at the same rate as the real term, giving rise to a diminished propagation velocity. It becomes apparent from the approximation analysis that the high-frequency solution causes the difference between the frequency-dependent hydraulics and the frequency-dependent streaming potential behavior. When the integral of equation (2.12) is evaluated, most of the contribution to the integral occurs along the wall of the capillary where most of the charge distribution is located. This region near the wall is also where the second-order effect of the hydraulic solution starts to dominate. Consequently, the frequency-dependent streaming potential exhibits high-frequency behavior that follows the form of the second-order effect of the hydraulic solution.
2.4 AC Streaming Potentials in Porous Media

A model for AC streaming potentials in a porous medium derived from first principles was developed by Pride\textsuperscript{12}. Pride’s version of the AC Helmholtz-Smoluchowski equation is given by

\[
CP(\omega) = \frac{\Delta V(\omega)}{\Delta P(\omega)} = \left[ \frac{\varepsilon \xi}{\eta \sigma} \right] \left[ 1 - \frac{i \omega \alpha m}{4 \left( 1 - 2 \frac{d}{\Lambda} \right)^2 \left( 1 - i \frac{\omega d}{\eta} \right)^2} \right]^{1/2},
\] (2.29)

where \( CP(\omega) \) represents the AC coupling coefficient for porous media using Pride’s model, \( d \) is the Debye length, and \( \Lambda \) is a typical pore radius representing a weighted volume-to-surface ratio\textsuperscript{19}. The transition frequency as defined by Pride\textsuperscript{12}

\[
\omega_t \equiv \frac{\phi \eta}{\alpha \kappa_0 \rho},
\] (2.30)

separates the low-frequency viscous flow regime from the high-frequency inertial flow regime. In Figure 2.2 the transition frequency occurs where the hydraulic imaginary curve intercepts the hydraulic real curve. Porosity is given by \( \phi \), tortuosity by \( \alpha \), and the DC permeability by \( \kappa_0 \). The dimensionless number \( m \) is defined as

\[
m \equiv \frac{\phi \kappa_0^2}{\alpha \kappa_0^2 \Lambda^2},
\] (2.31)

which is also a function of the pore microgeometry, which reduces to 8 for a capillary. Closer examination of the AC porous media coupling coefficient, equation (2.29), reveals that to a first-order approximation the response is determined by the transition frequency \( \omega_t \) and the DC coupling coefficient.
Figure 2.5 shows the normalized real and imaginary parts of the theoretical AC coupling for three capillaries of different radius using equation (2.16). The obvious characteristic of the curves is that the transition frequency shifts with changing radius of the capillary. This relationship is easily evident when looking at the equation for the transition frequency, equation (2.30) and realizing that the DC permeability for a capillary is
\[ k_o = \frac{a^2}{8} \]

The transition frequency for capillary then becomes
\[ \omega_t(\text{cap}) = \frac{8 \eta}{a^2 \rho} \]

2.5 Comparison of Packard’s and Pride’s Models

Pride\textsuperscript{12} generated his model by creating low-frequency and high-frequency models separately and then combining them into a single combined model. Equations (2.34) and (2.35) show Pride’s low-frequency and high-frequency models, respectively, when capillary geometry terms are used and second-order effects are neglected. Capillary geometry terms imply that \( m = 8, \phi = 1, \alpha = 1, \Lambda = a, \) and \( k_o = (a^2) / 8, \) where \( a \) is the capillary radius. Second-order effects occur when the Debye length is large compared to the capillary radius.

\[
CP_{LAC} = \frac{\varepsilon \xi^*}{\eta \sigma}
\]

\[
CP_{HAC} = -2 \left[ \frac{\varepsilon \xi^*}{\eta \sigma} \right] \frac{i^*}{\Lambda}
\]
Figure 2.5 - a) Normalized coupling coefficient of the real and imaginary component for three capillaries of different radii.
Equation (2.35) can be rewritten as

\[ CP_{\text{HAC}} = \left[ \frac{\varepsilon \zeta}{\eta \sigma} \right] \left[ \frac{-2}{a} \sqrt{\frac{\eta}{\rho \omega}} \sqrt{i} \right] \]  \hspace{1cm} (2.36)

where \( \delta \) is the viscous skin depth and is given by \((2\eta/\rho \omega)^{1/2}\). Equation (2.36) can also be rewritten as

\[ CP_{\text{HAC}} = \left[ \frac{\varepsilon \zeta}{\eta \sigma} \right] \left[ \frac{-2}{a} \sqrt{\frac{\eta}{\rho \omega}} \left( \frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} i \right) \right] \hspace{1cm} (2.37) \]

which clearly shows that the real and imaginary parts of the high-frequency solution are identical to equation 2.25 in the Bessel function approximation. One possibility of combining the low-frequency and high-frequency solutions into a single model is

\[ CP(\omega) = \left[ \frac{\varepsilon \zeta}{\eta \sigma} \right] \left[ 1 - \frac{2}{a} \sqrt{\frac{\eta}{\rho \omega}} \left( \frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} i \right) \right] \hspace{1cm} (2.38) \]

where capillary geometry is used and second order-effects are neglected.

The simplified version of Pride's model, equation (2.38), as opposed to the full equation, will be compared to Packard's equation for two reasons. First, the second-order effects do not affect the model within the range of frequency or concentrations for which Pride's model is defined. Second, the simplified model of Pride, equation (2.38), is identical to the approximated form of Packard's model equation (2.26). This implies, when using capillary geometry terms and neglecting second-order effects, that Pride's
model is identical to Packard's model when the series and asymptotic approximations are used.

A visual comparison of Packard’s and Pride’s models can be made by looking at Figure 2.4, where equation (2.16) and (2.38) are compared. A slight discrepancy between the two curves becomes apparent, which was addressed earlier in the paper. In order to completely approximate the Bessel function, the range where \( ka \) is greater than one but less than 10 must be addressed. Packard addresses this range because the Bessel function inherently covers the whole range. It appears from the comparison of the Packard’s Bessel function model to Pride’s model that Pride’s model does not completely address this region. When Figure 2.4 is compared to actual measurements, however it is difficult to resolve the difference between the two curves when experimental error is accounted for in the data. Consequently, Pride’s model is adequate in this region.

2.6 Experimental Approach

The approach used to collect the streaming potential data was to hold the capillary or porous filter stationary and oscillate the fluid back and forth through the sample using a sinusoidal driving pressure at one end while having the other end open to the atmosphere. Silver silver-chloride electrodes are placed on either side of the sample in fluid ports to keep them out of the fluid flow path\(^{22}\). The frequency response of the electrodes was measured using a four-electrode method and found to be flat in the region used in this experiment. The electrode measurements were also verified through the use of a capacitive coupled antenna placed around the outside of the sample. The pressure
was monitored on the high-pressure and atmospheric-pressure sides of the sample by miniature hydrophones that have a flat frequency response from 1-20 kHz. The acrylic apparatus, which holds the sample, electrodes, and hydrophones, is shown schematically in Figure 2.6. The enclosure around the sample and preamplifiers is constructed of Mu-metal. Mu-metal is used because of its superior electromagnetic shielding properties. The acrylic housing which holds the sample is additionally enclosed in an aluminum housing, and the electromechanical shaker that produces the driving pressure is enclosed in a separate steel box. This large quantity of shielding is required for two reasons. The first is that the laboratory is an electrically noisy environment. The second is that the pressure source is being generated by an electromechanical transducer, which is driven at the same frequency as the measured streaming potential. The driving transducer and associated leads emit enough electromagnetic signal (EMF) at the same frequency being measured to sometimes affect the measured results. Depending on the pore or capillary diameters, the resistance of the sample could be several hundred megaohms, which causes the sample to act as an antenna for the EMF fields produced by the electromechanical transducer. The acrylic housing had 50 kilograms of lead placed on it to reduce any sample vibration.

The waveforms were sampled using two instrument preamplifiers and a 12-bit analog-to-digital board with 24.8 microvolt resolution. Electrometers or FET preamplifiers are required as input buffers due to the high impedance of the samples (.5 MΩ to 1 GΩ). A schematic representation of the data acquisition system is shown in Figure 2.7. A Hanning window was applied to the data prior to spectral analysis. The
Figure 2.6 - A simplified schematic representation of the test cell and pressure source. The apparatus is constructed of Plexiglas and bolted to a heavy metal plate.
Streaming Potential Acquisition Circuit

Computer Data Acquisition
Electrodes

Preamplifier

Pressure Acquisition Circuit
Computer Data Acquisition
Hydrophone

Preamplifier

Figure 2.7 - A simplified representation of the data acquisition circuit is shown. Labview™ 12 bit AD board was used to acquire the data in the computer.
time-domain voltage and pressure were measured, and the amplitude spectrum ratios were also measured at the driving frequency. The raw data were saved for possible future processing. Cross-correlation analysis of the signals was also performed as a verification of the amplitude spectrum measurements.

2.7 Data/Results

In order to test Packard's and Pride's models experimentally, the pore diameters of the samples must be known. The pore diameter is used as an adjustable parameter in the models to fit the theory to the data. Actual pore diameters are then compared to the experimentally determined pore diameters. The pore diameters of the glass samples were provided by the manufacturer.

Capillary 1 has an inner diameter that ranges from 0.8 to 1.1 millimeters, and a length of 60 centimeters. Porous Filter A has a manufacturer-determined pore diameters ranging from 145 to 175 micrometers, an overall diameter of 1 centimeter, and a thickness of 2 millimeters. Porous Filter B has manufacturer-determined pore diameters ranging from 70 to 100 micrometers, an overall diameter of 1.9 centimeters, and a thickness of 1 centimeter.

The experiments were carried out using $10^{-3}$ M and $10^{-3.7}$ M KCl with a pH of 5.5. Assuming a concentration of $10^{-4}$ M KCl, the Debye length was found to be much less than the radius of the pore space. Therefore, second-order effects can be neglected in Pride's model.
Figure 2.8 shows the measurements of the coupling coefficient versus frequency for Capillary 1 along with a theoretical curve for equation (2.26). The data do not have a satisfactory fit to the theory. The frequency-dependent impedance of the sample and measuring circuit was determined and is shown in Figure 2.9. The RC of the circuit was found to have a resistance of 1 gigaohm and a capacitance of 25 picofarads. The resistance was determined to be on the order of the resistance of a 0.8 mm capillary filled with $10^{-3.7}$ M KCl. The capacitance was found to be on the order of the input capacitance of the amplifier and the capacitance of the wire leads. The data were then corrected for this impedance. The impedance of the sample and measuring circuit was determined using a four-electrode method. The normalized real and imaginary portions of the impedance at the particular frequencies of the streaming potential measurement were divided into the data. The corrected data are shown in Figure 2.10, where a good correlation between the theory and data is evident. At the higher frequencies, signal-to-noise problems caused the fit to have a little more scatter. The transition frequency determined from the fit of the theoretical curve is 7.1 hertz, which gives a capillary diameter of 0.8 millimeters. This is in agreement with the manufacturer-provided diameter of 0.8-1.1 millimeters for this type of capillary.

The corrected data for Porous Filter A, shown in Figure 2.11, are plotted against equation (2.26). As can be seen, the theory fits the data well. Fitting the theoretical curve to the data for Porous Filter A gives a pore radius of 65 micrometers and a transition
Figure 2.8 - Cross coupling real and imaginary uncorrected data for Capillary 1 plotted along with the theory for a 0.8 mm capillary.
Figure 2.9 – Capillary 1 impedance data plotted with the best RC circuit response. The resistance and capacitance of the RC circuit are 1 GΩ and 25 pF respectively.
Figure 2.10  Corrected cross coupling real and imaginary data for 60 mm long, 0.8 mm diameter capillary plotted along with the theory for a 0.8 mm capillary. Error bars are not shown because they fall within the size of the data points.
Figure 2.11 - Porous filter A corrected cross coupling real and imaginary data plotted with the theoretical response. The transition frequency was determined to be 269 Hz, which gives a pore radius of 65 micrometers.
frequency of 269 hertz. The manufacture-provided pore radii for the Porous Filter A is 72.5-87 micrometers.

Figure 2.12 shows the corrected data for Porous Filter B along with the best-fit theoretical curve. Porous filter B has its best fit to Pride’s theory, equation (2.26), using a 40 micrometer pore radius, and a transition frequency of 710 hertz. Recall that the pore radii provided by the manufacturer for Porous Filter B is 35 to 50 micrometers. The data for Porous Filter B fit the theory very well in the low-frequency and intermediate-frequency regions. At the higher frequencies, there is a little more scatter than at the low frequencies due to poor signal-to-noise ratio.

Figure 2.13 shows the data for a Boise Sandstone sample. The critical frequency for this sample is 5000 Hz. The permeability calculated from the critical frequency is found to be 2.89 Darcies. The measured permeability using the flow through technique was found to be 1.5 Darcies. The Boise sample had a lot of heterogeneity in it with a vein of large pore spaces running through it, which might explain the discrepancy in the permeability measurements.

It appears from the data that the experimentally determined pore radii tend toward low range of radii provided by the manufacturers. This may imply that the frequency-dependent streaming potential response is controlled by the smallest pore geometry in a fluid path.
Figure 2.12 – Porous filter B corrected cross coupling frequency response data plotted along with the theoretical response. The transition frequency was determined to be 710 Hz, which gives a pore radius of 40 micrometers. The manufacturer provided pore radius for porous filter B ranges from 35-50 micrometers.
Boise Sandstone

Figure 2.13 Boise Sandstone streaming potential coupling coefficient frequency response. The transition frequency is found to be at 5000 Hz.
2.8 Discussion and Applications

The emphasis of this study has been to examine for the first time, complex streaming potentials and to extend the frequency range covered by this type of experiment. As a consequence of this study Packard's and Pride's theories have been verified over a range of pore sizes. Both Packard's and Pride's theories fit the data nearly identically. The transition frequency is the important parameter to be determined uniquely, for both capillaries and porous filters, from frequency-dependent streaming potential curves. From the transition frequency the pore size can be determined. The transition frequency can be determined graphically from the data or by curve fitting the theory to the data and then determining the transition frequency from the theory. Packard's theory for a capillary is related to the capillary radius and the viscosity and density of the fluid. In Pride's model one additional parameter (m) is included, if the second-order parameters are neglected and Λ is taken as the pore radius. The second-order-effect parameters are important only where the pore sizes are very small and/or the electrolyte concentration is very low.

The data collected on glass filters with pore diameters much larger than the diffuse zone indicate that the curves generated using Pride's and Packard's theories cannot be distinguished from each other. This result confirms the analysis done earlier in the paper. What is different between the theories is that Pride's model includes second-order effects, which are eliminated in the approximation made during the solution of equation (2.16), Packard's model. In this respect, Pride's model appears to be more complete and general, but the accuracy in these regions has not been confirmed. From
the data thus far collected on porous filters, it can be concluded that the curves generated by Packard’s and Pride’s models can accurately fit the data. Therefore, both Packard’s and Pride’s models give identical results when used with realistic frequency ranges and solution chemistries as shown from the theoretical analysis and the experimental data.

2.9 Summary/Conclusion

Real and imaginary parts of frequency-dependent streaming potentials were measured for the first time. A comparison of streaming-potential data to proposed models has been presented for various pore sizes. Although there is a slight discrepancy between the capillary model and the generalized model, overall both Packard’s and Pride’s models fit the frequency-dependent streaming potential capillary data. For porous media, both Packard’s capillary model and Pride’s porous media model fit the data, which allows the pore size to be estimated. The difference between the two models comes from the model parameters used to fit the curve. When using Pride’s model, if either $m$ or $\Lambda$ are known a priori, it allows determination of the other parameter. From the results thus far presented, the frequency streaming potential response may be governed by the smallest pore geometry in the fluid path.

Currently plans are underway to extend the frequency range of the experiment to 20 – 30 kHz. This will allow study of a wider range of samples, including rocks. Studying a broader sampling of rocks will help us to understand the relationship between frequency dependent-streaming potentials and permeability as alluded to by others$^{16,17}$. A set of samples with well defined geometries will better help to confirm how well the
models can predict pore size and whether the response is governed by the pore-throat size. Lastly, performing frequency-dependent studies at higher temperatures and pressures will help us to ascertain what is happening to the solution chemistry and electrical double layer at in-situ temperatures and pressures for rocks. This understanding has importance to the oil industry as well as Earth scientists for the study of Earthquake nucleation\textsuperscript{23}.

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2.11 References


Chapter 3

Frequency-Dependent Electroosmosis

3.1 Introduction

Frequency-dependent electroosmosis (FDE) is studied because it has potential applications in the study of fluid flow in capillaries and porous media. Its counterpart, frequency-dependent streaming potentials, has been shown useful in determining capillary diameters and the pore diameters of porous media\textsuperscript{1,2}.

Frequency-dependent electroosmosis may have significant advantages over frequency-dependent streaming potentials, 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 because we are applying $\Delta V_m$ and measuring $\Delta P_a$.

The frequency-dependent electroosmosis coupling coefficient is the ratio of the voltage applied across the sample to the induced pressure measured across the sample ($\Delta V_a/\Delta P_m$). It has been found in this research that the FDE coupling coefficient also decreases as the frequency is increased past the critical frequency. There is a significant difference however, between the streaming potential and the electroosmosis cases. In the frequency dependent electroosmosis case, the voltage applied across the sample can be kept constant; 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 electroosmosis. Minor et al.$^3$ determined the characteristic time for dynamic electroosmosis and electrophoresis. They provided data showing the relaxation frequency and fitted the data with an empirically determined curve using the
characteristic time. According to Minor et al., there was not a good correlation between the theoretical and measured relaxation frequencies, although the general shape of the curves was in good agreement. There have been other recent papers on frequency dependent/dynamic electrophoresis\textsuperscript{4,5}, but they do not provide an analytical solution for the mobility. In the study of electroosmosis, 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 electroosmosis in a capillary. A brief review of DC electroosmosis is presented, followed by the development of frequency-dependent electroosmosis theory. Furthermore, experimental data collected by the author is presented to verify the theory.

### 3.2 Theory of DC Electroosmosis

DC electroosmosis has been studied in its present form, as presented by von Smoluchowski, for the past 79 years\textsuperscript{6}. In DC electroosmosis 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 water is moved by the electric field affecting 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{7} model of the electrical double layer is shown in Figure 3.1. The potential at the slipping plane is the zeta (\(\zeta\)) potential, the potential at the surface is \(\varphi_0\), and the potential at the Stern plane is \(\varphi_d\). It can be seen in Figure 3.1 that the potential decays exponentially from the Stern layer into the bulk fluid. This implies
Figure 3.1 – 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.
that there is excess charge near the Stern layer. Consequently, as the ions are moved near the surface by the electric field, viscous effects in the fluid pull the fluid along with the ions. This can be seen in Figure 3.2, which is a modified version of Hunter's figure. The equation governing DC electroosmosis is

\[ \eta \frac{\partial^2 \mathbf{v}_{\text{eDC}}(r)}{\partial r^2} = E \frac{\partial^2 \phi(r)}{\partial r^2}, \]  

(3.1)

where \( E \) is the electric field, \( \rho_c \) is the charge density, \( \eta \) is the viscosity of the fluid, \( \mathbf{v}_{\text{eDC}} \) is the DC electro-osmotic fluid velocity, and "r" is the distance from the surface. Equation (3.1) can be rewritten as

\[ E \rho_c dr = \eta \frac{d^2 \mathbf{v}_{\text{eDC}}(r)}{dr^2}, \]  

(3.2)

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

\[ \mathbf{v}_{\text{eDC}}(r) = -\frac{\varepsilon \zeta}{\eta} E \left[ \exp(-\kappa r) - 1 \right], \]  

(3.3)

where \( \zeta \exp(-\kappa r) = \phi(r) \). Equation (3.3) is usually approximated by

\[ \mathbf{v}_{\text{eDC}} = -\frac{\varepsilon \zeta}{\eta} E. \]  

(3.4)
Figure 3.2 – Simplified schematic representation of the electro-osmotic flow in open and closed capillaries. In the open capillary the electro-osmotic flow is shown as a plug flow which at its maximum velocity approximately 3 Debye lengths from the wall. In the closed capillary 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.
This approximation holds, when the velocity at a distance of three Debye lengths from the wall is essentially a constant. This can be seen by plotting equation (3.3). A plot of equation (3.3) is shown in Figure 3.3, 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 potential is reduced by a factor of 2.718 and is given by,

$$\kappa = \left(\frac{10^3(2Z^2 e^2 I_r N_A)}{\varepsilon k_B T} \right)^{\frac{1}{2}}, \quad (3.5)$$

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 number, $k_B$ is Boltzman's constant and $T$ is the temperature in Kelvins. The approximation made in equation (3.4) also holds because in electroosmosis one is usually dealing with fluid volumes. The fluid volume within three Debye lengths of the wall is infinitesimal compared to the volume in the bulk fluid, proving 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 electroosmotic volume flow. This is schematically seen in Figure 3.2b, which shows the electroosmosis flow and the counterflow are shown. The DC coupling coefficient is found by setting the electroosmosis volume flow equal to the counter volume flow and taking the ratio $\Delta V/\Delta P$, which gives

$$\frac{\Delta V}{\Delta P} = \frac{r^2}{8\varepsilon \zeta} \quad . \quad (3.6)$$
Figure 3.3 – This is a plot of the DC electo-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.
3.3 Theory of Frequency-Dependent Electroosmosis

Having done a brief review of DC electroosmosis, frequency-dependent electroosmosis will be examined. The equation governing frequency-dependent electroosmosis is

$$\rho \frac{\partial \dot{v}_e(r, \omega)}{\partial t} = \eta \frac{\partial^2 \dot{v}_e(r, \omega)}{\partial r^2} - \varepsilon \frac{\partial^2 \psi(r, \omega)}{\partial r^2} E_0 e^{i\omega t},$$  \hspace{1cm} (3.7)

where the first term is the fluid density multiplied by the acceleration of the fluid to give the inertial forces. The second term represents the viscous forces in the fluid, and the third term represents the forces due to the electric field. It can be seen that the second and third terms are the same as in the DC case except that now a time-varying driving function has been added. Equation (3.7) does not have an exact analytical solution because there is one equation and two unknowns, \( \dot{v}(r, \omega) \) and \( \phi(r, \omega) \). To find a solution for this equation it was solved for two different regions within the capillary, near the wall and in the bulk fluid. In order for these approximate solutions to be valid, certain restrictions are required.

The main restriction of this solution is that the viscous skin depth, \( \delta = \sqrt{\frac{\eta}{\rho \omega}} \),

$$\text{cannot approach within three Debye lengths of the wall. The solution is restricted to frequencies less then 1 MHz in solutions with concentrations greater than } 10^{-4} \text{ M. These}$$
restrictions ensure that there are no inertial effects within three Debye lengths of the wall. The viscous skin depth is the distance away from the no-flow boundary at the wall to where the vorticity wave has been attenuated by a factor of 2.718 (e). As part of this solution, it is assumed that the capillary is sufficiently long that end effects can be neglected.

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. The flow velocity is at its maximum in this region. As stated earlier in the discussion concerning the restrictions to the solution,

$$\eta \frac{\partial^2 v_{ew}(r, \omega)}{\partial r^2} = \varepsilon \frac{\partial^2 \psi(r)}{\partial r^2} E_0(\omega)e^{\text{tot}}, \quad \text{(3.9)}$$

there cannot be any inertial effects in the near-wall solution. Therefore, the governing equation for the near-wall solution becomes

which is essentially the DC solution with a time varying driving function. The solution of equation (3.8) is

$$v_{ew}(r, \omega) = \frac{\varepsilon \phi}{\eta} \left[ \exp(-\kappa r) - 1 \right] E_0(\omega)e^{\text{tot}}, \quad \text{(3.10)}$$

where $v_{ew}$ is the electro-osmotic velocity near the wall. Upon examination of equation (3.10) it can be seen that the velocity near the wall is always in phase with the driving electric field.
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 electroosmosis equation,

$$\rho \frac{\partial v_e(r, \omega)}{\partial t} = \eta \frac{\partial^2 v_e(r, \omega)}{\partial r^2} - \varepsilon \frac{\partial^2 \phi(r, \omega)}{\partial r^2} E_0 e^{i \omega t}, \quad (3.11)$$

which becomes

$$i \rho \omega v_e(r, \omega) = \eta \frac{\partial^2 v_e(r, \omega)}{\partial r^2} - \varepsilon \frac{\partial^2 \phi(r, \omega)}{\partial r^2} E_0 e^{i \omega t}. \quad (3.12)$$

Because we are dealing with only the bulk-fluid solution, a different set of boundary conditions now exists for the solution in the center of the capillary. This is because the potential distribution $\phi(r)$ drops to essentially zero in the bulk fluid, it can be concluded that

$$\frac{\partial^2 \phi(r, \omega)}{\partial r^2} \rightarrow 0. \quad (3.13)$$

In the bulk-fluid, equation (3.12) becomes

$$i \rho \omega v_{eb}(r, \omega) = \eta \frac{\partial^2 v_{eb}(r, \omega)}{\partial r^2}. \quad (3.14)$$

The boundary condition of the bulk-fluid solution requires that at three Debye lengths from the wall the velocity is at its maximum ($v_{em}$) and does not change with frequency. Rearranging equation (3.14), it takes the form
\[
\left[ \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + k^2 \right] v(r, \omega) = 0 ,
\]  
(3.15)

where

\[
k = \sqrt{-\frac{i \rho \omega}{\eta}} .
\]  
(3.16)

The general solution to Equation (3.15) has the form\(^8\)

\[
v(r, \omega) = C_1 J_0(3kr) + C_2 Y_0(3kr) ,
\]  
(3.17)

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

\[
v(r, \omega) = C_1 J_0(3kr) .
\]  
(3.18)

Applying the boundary condition that at 3/\(\kappa\) the velocity is \(v_{em}(r, \omega) = -\zeta/\eta E(\omega)\). \(C_1\) is determined to be

\[
C_1 = \frac{v_{em}(r, \omega)}{J_0(3ka)} ,
\]  
(3.19)

where “a” is the radius of the capillary. Substituting \(C_1\) into equation (3.18) the particular solution becomes

\[
v_{eb}(r, \omega) = -\frac{\zeta E(\omega)}{\eta} \frac{J_0(3kr)}{J_0(3ka)} .
\]  
(3.20)
The behavior of the velocity as a function of frequency and radial position in the capillary can be seen in Figure 3.4. 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 examine the frequency-dependent behavior of the electroosmosis coupling coefficient, the volume fluid flow must be determined. This is straightforward, achieved by integrating the fluid velocity in equation (3.18) over the cross section of the capillary, giving

\[ Q_e(\omega) = -2\pi E(\omega) \frac{\varepsilon \zeta a}{\eta} \frac{J_1(ka)}{k J_0(ka)} \quad \text{(3.21)} \]

where \( Q_e \) represents the electroosmosis volume flow.

**Counter-Flow Solution**

As shown in Figure 3.2b, a counter-flow must exist in a closed capillary. This counter-flow is driven by the pressure that builds up at the ends of the capillary and can be expressed as

\[ \rho \frac{\partial \mathbf{v}_c(r, \omega)}{\partial t} = \eta \frac{\partial^2 \mathbf{v}_c(r, \omega)}{\partial r^2} - \frac{\partial^2 P_0(\omega)}{\partial r^2} \mathbf{e}^{\text{tot}}, \quad \text{(3.22)} \]

where \( \mathbf{v}_c \) represents the counter-flow velocity and \( P_0 \) is amplitude of the driving pressure. Equation (3.22) indicates that the pressure forces are equal to the viscous forces minus
Figure 3.4 – This is a plot of the 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.
the inertial forces. Equation (3.22) has been solved numerous times in prior literature\textsuperscript{1,9,10}, with the solution given as

\[
v_c(r, \omega) = \frac{\Delta P(\omega)}{n/k^2} \left[ \frac{J_1(\epsilon kr)}{J_0(ka)} - 1 \right] ,
\]  

(3.23)

where \( l \) is the length of the capillary and \( k \) is the same as defined in equation (3.16). The volume flow is found by integrating counter-flow velocity over the area of the capillary to give

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

(3.24)

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

**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 \( \Delta V_a/\Delta P_m \). Setting \( Q_c \) equation (3.21) equal to \( Q_c \), (3.24), and taking the ratio \( \Delta V_a/\Delta P_m \) gives

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

(3.25)

which is the AC electroosmosis coupling coefficient in a closed capillary.

Graphically the real and imaginary response of the AC electroosmosis coupling coefficient for a closed capillary can be seen in Figure 3.5. The real part of equation (3.25) has a constant coupling coefficient until the critical frequency is reached, at which
Figure 3.5 – Real and imaginary portions of the electroosmosis frequency dependent coupling coefficient are shown for two different size capillaries.
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 Figure 3.6. It can also be seen by using two capillaries with radii of 100 µm and 500 µm that the critical frequency is dependent on the radius of the capillary. The frequency response of equation (3.25) can be better understood if one compares the frequency response of the electroosmosis volume flow to the counter volume flow. This is done graphically in Figure 3.7, where the counter volume flow drops off at a much faster rate with increasing frequency than the electroosmosis volume flow, thus giving the response shown in Figure 3.6.

3.5 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 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 μV/Pa. The voltages and pressure were monitored using a Labview® 12 bit AD board, and the signals were processed using Fourier analysis. The solution was 0.001 M KCl and had been allowed to achieve equilibrium with the capillary for a period of two weeks.
Figure 3.6 – The electroosmosis frequency dependent coupling coefficient phase response is shown for a 100 micron diameter capillary. The phase approaching 45 degrees at high frequencies is in agreement with the real and imaginary portions being equal in magnitude at the higher frequencies.
Figure 3.7- A comparison of the electro-osmotic and counter flow volume flow rates shows that the counter flow volume flow rate falls much faster than the electro-osmotic flow rate.
Figure (3.8) shows the frequency dependent electroosmosis 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 electroosmosis coupling coefficient, equation (3.25). Figure 3.8 shows that there is excellent agreement between the theory and the data.

3.5 Conclusion

The theory for frequency-dependent electroosmosis in a closed capillary has been presented, showing that the frequency-dependent behavior is a function of the pore diameter. This implies that frequency-dependent electroosmosis can be used to determine pore sizes of capillaries and porous media. The theory was compared to data collected using a 0.127 mm capillary and found to be in good agreement.
Figure 3.8 – Comparison of frequency dependent electroosmosis coupling coefficient data collected on a 0.127 mm capillary with the theoretical curve for the same capillary. There is excellent agreement between the data and the theory. The capillary had 0.001 M KCL solution as the electrolyte.
3.6 References


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Chapter 4

Applications of Frequency-Dependent Streaming Potentials and Frequency-Dependent Electroosmosis in the Earth Sciences

4.1 Introduction

Frequency-dependent streaming potentials (FDSP) and frequency-dependent electroosmosis (FDEO), collectively referred to as frequency-dependent electrokinetics (FDE) in the rest of this chapter, have several possible applications in the earth sciences. In the more general view of electrokinetics, electrophoresis can also have a frequency response, but electrophoresis is not included in the discussions of this chapter. These applications range from measurements of zeta potentials on rocks and soils, to
measurements of permeability, to the understanding and interpretation of the seismoelectric effects. Some of the applications of FDE are possible due to the fundamental nature of their hydrodynamics and or their electrochemistry. The applications in this chapter are not fully developed but are in their conception stage.

The rest of this chapter discusses both the benefits and the limitations associated with using frequency-dependent streaming potentials and frequency-dependent electroosmosis. This is followed by a section that examines the benefits and limitations of FDE, and how they may impact the fields of rock physics, permeability determination, and the seismoelectric effect. The last section examines the future work that needs to be done in order to increase our understanding and the application of frequency-dependent electrokinetics.

4.2 Benefits and Limitations

In the laboratory, there are several major advantages to using frequency dependent electrokinetics instead of using the traditional flow through streaming potential or electroosmosis techniques. The first and possibly the most important advantage is that the signal-to-noise ratio is orders of magnitude better than with the traditional techniques. A second advantage, almost as important, is that in streaming potential experiments, electrode polarization effects can be eliminated from measurements. This can be of importance when doing long experiments at elevated temperatures where the condition of silver silver-chloride electrodes may be questionable. Also, when using frequency-dependent techniques, DC electrode noise is not an issue. This directly helps to increase
the signal-to-noise ratio. Another advantage is that single measurements can be made to
determine coupling coefficients, as described by Reppert and Morgan [2000]. The
frequency methods also lend themselves to stacking of the data, which increases
repeatability of results as well as increasing the signal-to-noise ratio. The last significant
laboratory advantage for FDE using the frequency response of the streaming potential or
electroosmosis coupling coefficients is the ability to determine the pore size of the
sample [Packard, 1952; Pride, 1994; Reppert et al., 1998].

Frequency-dependent electroosmosis has many of the same advantages of
frequency-dependent streaming potentials, so only those advantages that are different will
be mentioned. Because the electric field driving the streaming current is sinusoidal,
gassing effects at the electrodes is minimized [Pengra et al., 1999]. If a constant-
amplitude electric field is maintained as the frequency is increased, the response of the
coupling coefficient requires that the measured pressure increase with increasing
frequency after the frequency has exceeded the relaxation frequency. This makes
monitoring the pressure measurements at frequencies above the relaxation frequency
easier. In FDSP, not only does the streaming-potential signal become smaller relative to
the pressure signal when measuring at frequencies higher than the relaxation frequency,
but limitations in the pressure driving devices make it difficult to generate measurable
pressure signals at high frequencies. This is especially true in the frequency range of 400
Hz to 5000 Hz.
There are some limitations to frequency-dependent streaming potentials; most can be worked around, but others may put restrictions on the use of this method. Whether the source driving the sinusoidal pressure is an electromechanical device or a piezoelectric device, an electromagnetic field (EMF) is emitted from the driving source. If the sample being tested has a high resistance, it acts like an antenna to the EMF, which may introduce error into the measurement. This problem can be minimized or eliminated by shielding the sample from the EMF [Reppert et al., 2000]. In certain instances, it may be possible to generate the pressure pulse manually and eliminate the source of EMF.

Another limitation associated with frequency-dependent streaming potentials is related to the frequency response. When frequencies approach 100 kHz, other effects start to occur in the fluid. At these frequencies, ultrasonic vibration potentials start to occur [Beck et al., 1978; Zana and Yeager, 1982]. The potentials associated with ultrasonic waves moving ions in an ionic fluid were first predicted by Debye [1933]. A very closely related phenomenon, colloidal potentials [Beck et al., 1978] is caused by the wave oscillating the ionic cloud around a colloidal particle. Consequently, at frequencies approaching ultrasonic frequencies, effects other than streaming potentials may be measured in addition to streaming potential signals.

The last limitation associated with frequency-dependent streaming potentials is directly associated with the frequency aspect of streaming potentials. When using a sinusoidal driving pressure, the driving frequency cannot have a wavelength on the same order as the length of the sample. Otherwise, standing waves may be generated between
the electrodes and pressure transducers. Because of standing waves, accurate coupling coefficients cannot be obtained. This problem can be circumvented by using traveling waves with the pressure source.

4.3 Implications of Frequency-Dependent Electrokinetics to Earth Science

In the rock physics laboratory, the benefits of frequency-dependent streaming potentials and frequency-dependent electroosmosis are clear. The superior-signal-to-noise characteristics allow the determination of coupling coefficients and zeta potentials on rocks in realistic conditions. Realistic conditions here refers to rocks that have not been cleaned and washed prior to testing, and it also refers to using realistic pore fluids. Under these conditions rocks tend to have much lower coupling coefficients and zeta potentials, making them difficult and sometimes impossible to measure using traditional methods. Therefore, realistic values of coupling coefficients and zeta potentials can be obtained for a variety of rocks in simulated in situ conditions.

A new method for determining the permeability of rock cores may now be available. In cases where the rock permeability is high and a limited amount of fluid is available, or the sample is very small, such as drilling chips for example, frequency-dependent streaming potentials and frequency-dependent electroosmosis may provide an interesting new alternative for determining the pore size and ultimately the permeability. However, this method may be restricted to measuring permeabilities greater than 1 mD or pore sizes larger than 6.6 microns in diameter. Pride [1994] first described that the pore
size of a porous media controls its streaming potential coupling coefficient frequency response, which was later demonstrated by Reppert et al. [2000]. This is readily seen in Figure 4.1, where a theoretical streaming potential frequency response is shown. Figure 4.1 shows that for a pore radius of 3.3 microns, the transition frequency is 100 kHz. The transition frequency is the frequency at which inertial effects start to dominate over viscous effects in the bulk fluid of the pore and is given by

$$\omega_t = \frac{\omega}{k_o} \frac{1}{F} ,$$  \hspace{1cm} (4.1)

where $\omega$ is the angular frequency, $\eta$ is the viscosity of the fluid, $\rho$ is the density of the fluid, $k_o$ is the DC permeability, and $F$ is the formation factor, defined as

$$F \equiv \frac{\alpha_e}{\phi} ,$$  \hspace{1cm} (4.2)

Figure 4.2 shows plots of the transition frequency versus permeability $k_o$ for several formation factors. It can be seen in this figure that for a frequency of 100 kHz the smallest permeability for which a transition frequency can be measured is 1 mD. If we look back at Figure 4.1 however, the relaxation in the curve actually starts to occur around 900 Hz, which is significantly below 100 kHz. Consequently, enough data points can be collected prior to reaching 100 kHz to allow the pore size and permeability to be determined.

Some of the lessons we have learned in the laboratory can be applied to the seismoelectric effect. We have learned that streaming-potential signals coming from
Figure 4.1  Real and imaginary components of the streaming potential coupling coefficient response for a 3.3 μm pore diameter. The transition frequency is at 100 kHz.
Figure 4.2   The transition frequency is plotted versus permeability for four different formation factors.
dirty rocks are generally small. We have also learned that in very permeable rocks streaming potentials may be reduced even further because the diminished response for frequencies greater than the relaxation frequency. On the other hand a large majority of rocks have pore sizes so small that no diminished signals will be encountered other than in relatively large fractures. In the frequency range of most seismic experiments it is doubtful that the frequency response of frequency-dependent streaming potentials would provide any additional information. However, there are a few cases, such as pointed out by Mikhailov et al. [1998], where the seismoelectric effect has shown some possible usefulness in finding fractures and permeable zones in and near a borehole. These measurements were made in a borehole using Stonley waves. The low frequency (long-wavelength) measurements appear to correlate with the theoretical predictions. The higher-frequency data however, do not have a good correlation with the expected results. It appears that the problem may be related to not having accurate measurements of pressure and streaming potentials.

Earlier in this section, the idea of using frequency-dependent streaming potentials and frequency-dependent electroosmosis to determine permeability in the laboratory was mentioned. A potentially much more useful application however, would be to use frequency dependent streaming potentials and frequency-dependent electroosmosis to determine in situ permeability. Because of the previously discussed limitations associated with possibility of using FDE methods to determine permeability, the discussion of permeability will be limited to permeabilities larger than 1 millidarcy. This restriction limits the use of the method to near-surface situations except for the unusual
exception where larger than normal permeabilities are encountered at moderate depths. Possible applications that meet this criterion include aquifers [Molch and Sayed, 1995] and certain parts of earthen dams [Corwin, 2000 personal communication]. Being able to monitor permeability is of great importance in both of these applications. In earthen dams monitoring programs are being developed with the intention of detecting leaks prior to catastrophic failure of the dam. One possible method of accomplishing this is to monitor the permeability of the saturated zone on the upstream side of the impermeable boundary in the center of the dam. Any seepage paths that have higher seepage rates will wash the fines out of the pore spaces, thus increasing the pore size. If this increased pore size can be detected by the use of FDE, repairs can be made on the dam prior to failure.

Two possible methods for doing in situ permeability measurements are borehole-to-borehole and down borehole. The down-borehole method could use a device physically similar to the device designed by Chandler and patented in 1981, or it could use a method similar to Mikhailov’s [1998]. A device similar to Chandler’s would make two seals against the borehole wall at a specified distance apart; each sealed area would have a hydrophone and an electrode contained in the fluid next to the wall. A high-frequency transient would then be generated in the one sealed area and the differential pressure and voltage between the two sealed areas would be measured. The coupling coefficient could then be calculated over the desired frequency range.

Using the method of Mikhailov, a pressure gradient is generated using a Stonley wave. The resultant streaming potential signal can then be measured in the borehole as
well as on the surface. Applying self-potential modeling techniques and values estimated for zeta potentials, quantitative values for fluid flow and ultimately permeability can be established. It should be noted that there are frequency limitations when using the Stonley wave: a maximum frequency of approximately 300-500 Hz can be used because of wavelength considerations.

The borehole-to-borehole method has one technological hurdle to overcome in order to become a useful means of determining permeability. At the present time, streaming potential coupling coefficients can be measured at high frequencies using sinusoidal sources, because of the issues associated with standing waves. If pulses (wavelets) are used it may be possible to measure coupling coefficients at high frequencies. As the wavelet passes through the fluid-saturated rock, both the rock and the fluid move together except for the differences in the bulk and elastic moduli between the rock and the fluid [Haartsen et al., 1998]. These differences cause the relative motion between the rock and the pore fluid. Measuring the pressure difference associated with this flow is problematic. One possible approach might be to use the attenuation of the wavelet as a measure of how much energy is lost because of the differences in bulk and elastic moduli between the pore fluid and the rock. Then, using the theory of Haartsen, it may be possible to calculate a differential pressure associated with the streaming potential signal.
4.4 Future Work

There are several research areas where continued work on frequency-dependent streaming potentials and frequency-dependent electroosmosis will be beneficial. In addition, in the application of FDE, continued work on equipment and techniques may make frequency-dependent streaming potentials and electroosmosis more useful in field situations.

Future work in the area of frequency dependent streaming potentials should include:

- Understanding the transient and wavelet technique of measuring streaming potential coupling coefficients
- Attempting to make coupling coefficient measurements in the range of 10-20 kHz, to aid in the understanding the problems associated with standing waves and wavelets.
- Pushing our understanding further as to how permeability relates to the pore structure and the measured frequency response. Making very controlled samples with precisely known geometries and measuring the permeability of these samples using the transition frequency of frequency-dependent streaming potentials.
- Creating high-frequency, high-pressure transients.

Future work in the area of frequency-dependent electroosmosis should include:

- Understanding the electromagnetic (EM) coupling effects that may occur at high frequencies.
• Developing ways to mitigate any EM coupling effects that may occur.
• Pushing our understanding further as to how permeability relates to the pore structure and the measured electro-osmotic frequency response. Making very controlled samples with precisely known geometries and measuring the permeability of these samples.

4.5 Conclusion

Despite some limitations, frequency-dependent streaming potentials and frequency dependent electroosmosis do have applications in the earth sciences. At the present time most of these applications are in the laboratory, with only limited applications in the field. With continued work however, further field applications may start to become available.
4.6 References


Chapter 5

Streaming Potentials at Elevated Temperatures: Theory and Review

5.1 Introduction

Recently the geophysical community has expressed a renewed interest in streaming potentials [Reppert et al., 2000; Pengra et al., 1999; Revil et al., 1999; Lorne et al., 1999; Reppert and Morgan, 1999;]. Advances in geophysical inversion and modeling techniques [Shi, 1998; Sai and Morgan, 1997; Warmstich and Morgan, 1994] have made it possible to measure as well as interpret streaming potential data.
One aspect of this renewed interest appears to be related to determining pore geometry from streaming potentials [Reppert et al., 2000; Pengra and Wong, 1999; Reppert et al., 1998; Jouniaux and Pozzi, 1995]. A second aspect of this renewed interest appears to be related to the possibility of using streaming potentials to monitor underground fluid flow and the rock/fluid interfacial chemistry [Revil et al., 1999a, 1999b; Reppert and Morgan, 1999]. This chapter examines the temperature-dependent relationship between streaming potentials and the interfacial chemistry of the rock/fluid system.

The study of streaming potentials at elevated temperature and pressure has applications for the earth sciences in at least two different areas of research. The first area is in the field of geothermal exploration. As the status of the world’s oil reserves continues to be unpredictable [Reynolds, 1999], the use of geothermal energy can become an attractive alternative in regions where it is available. Measurement of self-potentials in geothermal areas provides an interesting means for investigating the subsurface fluid flow. Streaming potentials as large as +2.3 volts have been measured over the Kilauea geothermal area in Hawaii by Zablocki [1976]. Apostopoulos et al. [1998] reported measurements in the -500 mV to +300 mV range. Morgan et al. [1989] concludes that simple order-of-magnitude estimates of thermoelectric and diffusion effects requires that streaming potentials be the major contributor to these voltages in geothermal regions. Ishido and Mizutani [1981] present one of the first attempts at relating streaming potentials in geothermal regions back to the rock/fluid chemistry. Ishido et al. [1983], attempted to monitor subsurface flow in a geothermal region.
using measurements of streaming potentials. Geophysical inversion techniques [Fitterman and Corwin, 1982; Sill, 1983] attempted to provide subsurface interpretation for surface streaming potential measurements. Shi [1998], Shi and Morgan, [1996] significantly improved the streaming potential inversion by including resistivity and constraints in 3-D.

Recent advances in measuring and modeling streaming potentials in the earth have made significant steps toward understanding fluid flow in geothermal regions. The theoretical prediction of the variation of streaming potential coupling coefficients with temperature is still in its infancy. Ishido and Mizutani [1981] did experiments at low temperatures and tried to model the parameters that govern the coupling coefficient based on their data. Revil et al. [1999a, 1999b] present a theory for zeta potentials, which is the coupling-coefficient parameter least understood with regards to temperature. Realistic numbers for streaming potential coupling coefficients still do not exist for the temperatures and pressures found in geothermal regions, and thus the models cannot be verified.

Another area of research that requires an understanding of the temperature-dependent behavior of streaming potential coupling coefficients is earthquake prediction. It has been suggested that electromagnetic events are often associated with earthquakes [Mizutani et al., 1976; Nitsan, 1977; Stoker and Warwick, 1982; Lockner et al., 1983, Varotsos and Alexopoulos, 1984; Johnston, 1989; Morgan et al., 1989; Draganov et al., 1991; Park et al., 1993, Porov et al., 1995, Park, 1996; Korepanov, 1998; Enescu et al.,
There are several theories as to the cause of these electromagnetic phenomena. Some researchers suggest piezoelectric effects in the rocks [Nitsan, 1977; Ogawa et al., 1985]. Cress et al. [1987] conclude that exoelectron bombardment of the fluid in the rock is the source of the electromagnetic radiation. Mizutani et al. [1976], Morgan et al. [1989], and Draganov et al. [1991] suggest streaming potentials as the possible source of EM events associated with earthquakes. Lastly, Morgan [1995] suggests an electrical double layer (EDL) squirt phenomenon, where the water and charge of the electrical double layer are squirted out of the pore as it collapses under pressure and Van der Waals forces completely close the pore or crack.

In order to understand which of these mechanisms is the most likely candidate for causing the electromagnetic precursors, the rock conductivity and the pore fluid conductivity as well as the electrical double layer of rocks must be understood at elevated temperatures and pressures. Can the zeta potential be large enough to support the streaming potential theories? Can the rock/solution interface acquire enough charge to support the EDL squirt theory? Or is this phenomenon unrelated to streaming potentials and the electrical double layer? A first step in answering these questions is to understand streaming potential coupling coefficients at elevated temperatures.

In this chapter, a condensed version of streaming potential theory is presented and is then followed by a review of the experimental work done on streaming potentials at elevated temperature. The review is then followed by a development of the theory of streaming potentials at elevated temperature.
5.2 Theory of Streaming Potentials

Streaming potentials occur when there is relative motion between a rock and the pore fluid inside the rock. This phenomenon is due to the charge distribution that occurs at the interfacial boundary. Consequently, all streaming potentials are intimately related with the electrochemistry of the rock/solution interface.

Several models are available to describe the charge distribution at the interfacial boundary [Bockris and Reddy, 1970]. One of the simplest models describing the electrical double layer is the Gouy-Chapman model, consisting of a charged surface with a diffuse charge layer decaying away from the surface. The Stern model [Stern 1924], shown in Figure 5.1a, divides the electrical double layer (EDL) into two parts; the Helmholtz layer and the diffuse layer. Figure 5.1a shows three planes of interest in the charge distribution of the Stern model. The three planes are the surface; Stern plane, or outer Helmholtz plane (OH); and the slipping plane (S). Figure 5.1b shows two possible potential distributions, and the potentials associated with these three planes of the Stern model. The potential associated with the surface is designated \( \varphi_0 \). The Stern plane (OH) is the plane where the diffuse layer starts and extends into the bulk fluid; the potential associated with the Stern plane is designated \( \varphi_d \). The slipping plane is the plane where the fluid velocity goes to zero when the fluid motion is tangential to the surface. The potential at this plane is referred to as the zeta potential, designated \( \zeta \). The EDL model used in the remainder of this chapter is the Stern model, with the assumption that there is no charge between the Stern plane and the surface. This model essentially has a Gouy-Chapman charge distribution starting at the Stern plane instead of the surface.
Figure 5.1 - a) Simplified schematic representation of the electrical double layer where (OH) is the outer Helmholtz or Stern plane, and (S) is the slipping plane, the diffuse zone is represented by diminished number of ions. b) Simplified schematic representation of the potential distribution in the electrical double layer, where $\phi_0$ is the potential at the surface, $\phi_d$ is the potential at the Stern plane, and $\zeta_1$ is the potential at the slipping plane for the Stern model and $\zeta_2$ is the potential at the slipping plane for the Stern model with the assumption that there is no charge in the region between the (OH) and the surface. The simplified Stern model varies linearly between the surface and the Stern plane and it varies exponentially into the bulk fluid.
The Gouy-Chapman model does not take into account the finite size of ions, and consequently allows the diffuse layer to start at the surface, whereas the Stern model takes into account the finite size of ions.

As the fluid moves tangentially to the surface, it pulls ions along in the vicinity of the slipping plane, developing a convection current \( I_{\text{conv}} \). This current can be seen schematically in Figure 5.2 where the fluid motion is shown going to the right in the capillary, pulling the ions along in a convection current. The definition of the convection current is

\[
I_{\text{conv}} = \int \rho_c v_n \, dr ,
\]

(5.1)

where \( v_n \) is the component of the velocity of the liquid normal to \( dr \) and \( dr \) is an infinitesimal part of the cross section, and \( \rho_c \) is the charge density. [Overbeek, 1952]. To derive the convection current in a capillary, we start with the Navier-Stokes equation in cylindrical coordinates,

\[
\rho \frac{\partial \mathbf{v}(r)}{\partial t} = -\nabla P + \mathbf{B} + \eta \nabla^2 \mathbf{v}(r) ,
\]

(5.2)

where \( \rho \) is the fluid density, \( \nabla P \) is the pressure gradient, \( \mathbf{B} \) is the gravitational body force, \( \eta \) is the fluid viscosity, and \( \mathbf{v} \) is the fluid velocity. The Navier-Stokes equation is then solved for fluid velocity in a capillary, giving the Hagen-Poiseuille equation.
Figure 5.2 – Simplified model of streaming currents in a capillary where “2a” is the diameter of the capillary, $l$ is the length of the capillary.
\[
v(r) = \frac{1}{4\eta} \frac{\Delta P}{l} \left( r^2 - a^2 \right) . \tag{5.3}
\]

The Hagen-Poiseuille equation is then used as the fluid velocity in the convection current equation, equation (5.1), giving

\[
I_{\text{conv}} = \int \frac{1}{4\eta} \frac{\Delta P}{l} \left( r^2 - a^2 \right) \left[ -\varepsilon \frac{\partial}{\partial r} \left( r \frac{\partial \Psi(r)}{\partial r} \right) \right] dr , \tag{5.4}
\]

where the charge density,

\[
\rho_e = -\varepsilon \nabla^2 \psi(r) = -\varepsilon \frac{\partial}{\partial r} \left( r \frac{\partial \Psi(r)}{\partial r} \right) , \tag{5.5}
\]

is given by Poisson's equation in cylindrical coordinates, \( \varepsilon \) is the permittivity of the fluid and \( \Psi(r) \) is the potential. The solution of equation (5.4) gives

\[
I_{\text{conv}} = \frac{\pi a^2 \varepsilon \zeta \Delta P}{\eta l} , \tag{5.6}
\]

where equation (5.4) has been integrated from the center of the capillary to where the fluid stops moving adjacent to the wall. This location is often referred to as the slipping plane; the potential there is the zeta (\( \zeta \)) potential. The permittivity of the fluid is denoted as \( \varepsilon \), \( \eta \) is the fluid viscosity, \( l \) is the length of the capillary, and \( \Delta P \) is the pressure difference across the capillary.
Under steady-state equilibrium conditions the convection current must be balanced by a conduction current. The conduction current is determined using Ohm's law, where

\[
I_{\text{cond}} = \frac{\Delta V \pi a^2 \sigma}{l}. \tag{5.7}
\]

Setting the convection current and conduction current equal to each other (equations 5.6 and 5.7) the streaming potential, \(\Delta V\), is determined to be

\[
\Delta V = \frac{\varepsilon \zeta}{\eta \sigma} \Delta P. \tag{5.8}
\]

Equation (5.8) can be rearranged by taking the ratio of the voltage difference to the pressure difference, giving us the Helmholtz-Smoluchowski equation,

\[
\frac{\Delta V}{\Delta P} = \frac{\varepsilon \zeta}{\eta \sigma}. \tag{5.9}
\]

For the rest of this chapter \(\Delta V/\Delta P\) is referred to as the *streaming potential cross-coupling coefficient*, or simply, the *coupling coefficient* (CC). It should be noted that the Helmholtz-Smoluchowski equation is absent of any geometric terms and applies to both capillaries and porous media as pointed out by Overbeek [1952] and Pride (1994).
When the pore width approaches the dimensions of the diffuse layer, surface conductance effects must be considered in the Helmholtz-Smoluchowski equation, given by

\[
\frac{\Delta V}{\Delta P} = \frac{\varepsilon \zeta}{\eta} \left\{ \frac{1}{\sigma + \frac{2\sigma_s}{a}} \right\},
\]

where \(\sigma_s\) is the surface conductance, [Overbeek, 1952; Morgan, et. al., 1989]. Surface conductance effects become important when the pore size is on the order of several Debye lengths. Debye lengths range from 96 nanometers for \(10^{-5}\) molar solution to 0.96 nanometers for \(10^{-1}\) molar solution.

### 5.3 Literature Review

The field of temperature-dependent and pressure-dependent streaming potentials has not generated many papers in the past. In the last 52 years, there have been nine papers that provide data on temperature-dependent streaming potentials. No papers were found dealing with the pressure dependence of streaming potentials. The papers reviewed in this section are reviewed in the order in which they were published. In some of the papers, zeta potentials were reported instead of streaming potential coupling coefficients.

Prior to starting this review, the streaming potential cross-coupling coefficient (Helmholtz-Smoluchowski equation), is rewritten to show the explicit temperature dependence.
\[ CC(T) = \frac{\Delta V(T)}{\Delta P(T)} = \frac{\varepsilon(T) \zeta(T)}{\eta(T) \sigma(T)} \] \hspace{1cm} (5.11)

Where \( CC(T) \) is the temperature-dependent cross-coupling coefficient, \( \Delta V(T) \) is the temperature-dependent voltage measured across the sample, \( \Delta P(T) \) is the temperature-dependent pressure measured across the sample, \( \varepsilon(T) \) is the temperature-dependent permittivity, \( \zeta(T) \) is the temperature-dependent zeta potential, \( \eta(T) \) is the temperature-dependent viscosity, and \( \sigma(T) \) is the temperature dependent fluid conductivity. As can be seen, every quantity in this equation can in principle have a temperature dependence.

Buchanan and Hayman [1948] performed a study on the electrokinetic potential of sparingly soluble sulfates. As part of the study, they reported no variation in the zeta potential greater than the experimental accuracy in the temperature range of 15 to 25°C. Their experiments were conducted using a flow through apparatus on barium sulfate while keeping concentration and pH constant.

Schriever and Bliel [1957] reported an increase in the magnitude of coupling coefficients and the magnitude of zeta potential with increasing temperature as determined from their studies on glass [Figure 5.3]. Their studies were conducted on spherical glass beads in doubly distilled water. The temperature was varied from 25 to 45°C. The experiment was conducted using a flow-through technique while keeping the concentration and pH of the fluid constant. They determined that the temperature dependence of the streaming potential coupling coefficient fits the empirical equation
Figure 5.3 – Coupling coefficient data of Schriever and Bliel [1957]. The data was collected on glass beads in distilled water.
\[
\frac{\Delta V}{\Delta P} = \left( \frac{V}{P} \right)_{25} (1 + \beta (\theta - 25))
\] .

(5.12)

Where \(\Delta V/\Delta P\) is the streaming potential coupling coefficient, \(\beta\) is a constant found by the method of least squares to be \(5.35 \times 10^{-2} \degree C\), and \(\theta\) is the temperature. They also developed an empirical relationship for the zeta potential,

\[
\zeta = \zeta_0 (1 + (\alpha + \gamma)\theta + (\alpha \gamma + \gamma^2 + b)\theta^2)
\] ,

(5.13)

which has a positive temperature coefficient of \(0.039/\degree C\) where \(\gamma\) is the temperature coefficient for the permittivity and \(\alpha = 3.4 \times 10^{-2}/\degree C\) is a constant that was determined experimentally. \(\theta\) is the temperature and \(b\) is another constant. The zeta potential temperature coefficient is determined from the slope of the line given by Equation (5.13), where the zeta potential coefficient equals the quantity of \((\alpha + \gamma)\), which has a value of \(3.9 \times 10^{-2}/\degree C\). They concluded that the changes in streaming potential and zeta potential are explained by the combined effect of changes in permittivity, viscosity, conductivity, and zeta potential with temperature.

Somasundaran and Kulkarni [1973] performed streaming potential measurements on several samples as part of a demonstration of a new streaming potential apparatus. However, they did not report their findings in the form of coupling coefficients versus temperature but rather zeta potentials versus temperature. Their three samples, quartz, sapphire alumina and hematite all show an increase in the magnitude of the zeta potential with increasing temperature [Figure 5.4]. They also varied concentration and pH with temperature and showed that zeta potential
Figure 5.4 – Zeta potential data of Somasundaran and Kulkarni [1973].
had a nonlinear response to changes in pH and concentration. Their experiments were conducted on a flow-through apparatus using platinum electrodes. Note that platinum electrodes can cause erroneous results in streaming potential experiments [Zucker, 1959 and Morgan et al., 1989]. During each test they maintained constant concentration and pH as they varied the other quantities. The test cell was immersed in a water bath in order to maintain a constant temperature, and they varied the temperature from 25°C to 90°C. Their samples were made of crushed rock. They concluded that the minerals became more negatively charged as temperature increases. They also concluded that the magnitude of the streaming potentials increase with temperature.

Ishido and Mizutani [1981], in an influential paper on the experimental and theoretical basis of electrokinetic phenomena in rock/water systems and its application to geophysics, made streaming potential measurements on quartz as a function of temperature, with the electrolyte consisting of KNO₃. They reported their results as coupling coefficient versus temperature [Figure 5.5] and zeta potential versus temperature [Figure 5.6]. It can be seen in these results that the magnitudes of both streaming potentials and zeta potentials increase with increasing temperature. They also showed another data set of zeta potential versus temperature on quartz. This time they used an electrolyte composed of Al(NO₃)₃ and KNO₃. This result showed the zeta potential increasing with temperature from 30°C to approximately 55°C, at which point the zeta potential started to decrease [Figure 5.6]. In general their experiments had a temperature range of 18°C to 75°C, and they maintained constant concentration and pH as they varied the temperature. The experiments were conducted in a flow-through
Figure 5.5 – Coupling coefficient data of Ishido and Mizutani [1981].
Figure 5.6 – Zeta potential data of Ishido and Mizutani [1981]. The theory of Ishido is shown annotated with its slope.
apparatus, which was immersed in a constant-temperature bath. Ishido and Mizutani (1981) presented a theory for the temperature dependence of zeta potentials in which they make the assumption that the solution is dilute and therefore the Gouy-Chapman model of the electrical double layer can be used. This assumption then allows them to approximate the zeta potential. They utilized a relationship developed in an earlier paper Ishido (1977) that relates pH to surface potentials,

\[ \Delta \text{pH} = \frac{-e\phi_o}{2.3kT}, \] (5.14)

where \( \Delta \text{pH} \) is the pH minus the iso-electric point. They then used this equation to solve for the surface electric potential \( \phi_o \), where \( k \) is the Boltzmann constant and \( T \) is temperature in °K. Once \( \phi_o \) is calculated, the zeta potential can be calculated by solving for \( \phi(x) \) at the slipping plane, using equations (5.15) and (5.16) as given by Overbeek (1952).

\[ \phi(x) = \frac{2kT}{ze} \ln \left( \frac{1 + \Psi \exp(-\kappa x)}{1 - \Psi \exp(-\kappa x)} \right), \] (5.15)

which gives the potential at a distance \( x \) from the surface, where

\[ \Psi = \frac{\exp(ze\phi_o/2kT) - 1}{\exp(ze\phi_o/2kT) + 1}, \] (5.16)

and \( \kappa \) is the Debye screening length, \( z \) is the valence of the ion, \( e \) is the charge, and \( T \) is the temperature in K. The value of \( x \) is the distance into the solution from the solid liquid interface. Because the exact distance of the slipping plane from the surface is not known, \( x \) is used as an adjustable parameter. From their calculations, they determined that for
quartz in an aqueous solution of $10^{-3}$ N KNO$_3$ with a pH of 6.1 there is an increase in the zeta potential of 3.3 mV/10°C [Figure 5.6]. Their solution had good results but seems to lack the detail to handle more complicated systems. In 1983, Ishido, Mizutani, and Baba applied their theory of 1981 to streaming potential measurements at geothermal fields. This work did not modify their earlier theory, but applied their earlier theory to field results.

Alekhin, et al. [1985] conducted several experiments on two samples using various electrolytes in order to examine adsorption properties. They showed zeta potential versus temperature for a SiO$_2$ system using 0.001 M NaCl with a pH of 4. The data showed a linear increase in zeta potential with temperature [Figure 5.7]. They also showed several data sets for Al$_2$O$_3$ with various solution compositions. The Al$_2$O$_3$ zeta potential results did not remain linear but changed from a linear response to a nonlinear response for some but not all, of the solutions examined. Their paper provided limited information on their experimental setup and procedures. It was shown only in their figures that the temperature range was from 25°C to 250°C and that they maintained a pore pressure of 7-8 MPa during the experiments. From the figures, it also appears that the experiment was performed using the flow-through method.

Morgan, et al. [1989] presented streaming potential coupling coefficient data versus temperature as part of a paper on streaming potential properties of Westerly Granite. These were collected on crushed Westerly Granite using NaCl as the electrolyte. The measurements show a decrease of the coupling coefficient with increasing
Figure 5.7 – Zeta potential data of Alekhin et al., [1985].
temperature [Figure 5.8]. It was pointed out in the paper that when the changes of permittivity, viscosity, and conductivity with temperature were accounted for, the zeta potential did not vary with temperature. This experiment was conducted using flow-through apparatus for measuring streaming potentials while the concentration and pH were maintained constant.

Jayaweera, et al. [1993] performed high-temperature streaming potential measurements on a variety of oxides to examine oxide properties. They did not show or discuss any data sets where they varied the temperature in order to get streaming potential coupling coefficient data or zeta potential data versus temperature. They did find in their conclusions for oxides however, that the absolute values of zeta potentials at high temperature are typically higher than at ambient temperature [Figure 5.9]. These experiments were conducted in a flow-through apparatus using platinum electrodes where the pH and concentration were kept constant. The temperature range was from 23°C to 235°C. Their experiments were obviously conducted under pressure.

Dunstan [1994] did electrophoretic measurements on silica and alkane colloidal particles in water and KCl in order to determine zeta potential versus temperature. These experiments were carried out over a temperature range from 10°C to 60°C at atmospheric pressure while pH and concentration were maintained constant. The results show that the zeta potential for silica decreases for both electrolytes, while the alkane zeta potential increases for both electrolytes [Figure 5.10].
Figure 5.8 -- Coupling coefficient data of Morgan et al., [1989].
Figure 5.9 – Zeta potential data of Jayaweera et al., [1993].
Figure 5.10 – Zeta potential data of Dunstan [1994].
Schwartz et al. [1994] performed streaming potential measurements on porous polysulfone membranes. They concluded that in the temperature range of 20 to 70°C a temperature dependence of the zeta potential could not be observed. The measurements were conducted using 0.001 M KCl solutions.

Pengra et al. [1999], as part of a study on low-frequency electrokinetics, made measurements while varying temperature in the range of 5-50°C. They found small increases in the streaming potential coupling coefficient for Fontainebleau Sandstone and fused glass beads [Figure 5.11]. Slightly larger increases were observed for Berea Sandstone and Indiana Limestone [Figure 5.11]. The experiments were conducted using 0.1 M NaCl brine in a non-flow-through apparatus. From their discussion it does not appear that values of the streaming potential coupling coefficient are equilibrium values.

Table 1 shows a comparison of the papers reviewed above. As can be seen in this review, no particular pattern emerges as to the temperature dependence of streaming potential coupling coefficients or zeta potentials. Figure 5.12 shows plots of all the zeta potential versus temperature data from the different papers combined in one figure and Figure 5.13 shows the plots for zeta potentials which were made using experiments on earth type materials and chemistries. The zeta potentials that are for materials and chemistries representative of the earth are marked with an asterisk in the legend of figure 5.12. In reviewing the above works, one major point should be noted. All but two of the experiments were conducted at
Figure 5.11 – Coupling coefficient data of Pengra et al., [1999].
### Table 5.1 – Comparison of papers in the reviewed, where CC stands for coupling coefficient section

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Measurement Technique</th>
<th>Plots Shown in Paper</th>
<th>Surface &amp; Solution Chemistry</th>
<th>Temp. Range</th>
<th>Pressure Range</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buchanan and Hayman</td>
<td>1948</td>
<td>Flow through Streaming Potential</td>
<td>CC vs T, ζ vs T</td>
<td>BaSO₄</td>
<td>15-25°C</td>
<td>Atm. Pressure</td>
<td>No change in ζ with change in T</td>
</tr>
<tr>
<td>Schriever and Bliel</td>
<td>1957</td>
<td>Flow through streaming Potential</td>
<td>CC vs T, ζ vs T</td>
<td>Glass Beads, Distilled Water</td>
<td>25-45°C</td>
<td>Atm. Pressure</td>
<td>Developed empirical equations for ζ and CC CC shows an increase with increasing T</td>
</tr>
<tr>
<td>Sosmasundaran and Kullarni</td>
<td>1973</td>
<td>Flow through Streaming Potential</td>
<td>ζ vs pH, ζ vs T</td>
<td>Al₂O₃, Quartz, Hematite KNO₃</td>
<td>25-90°C</td>
<td>Atm. Pressure</td>
<td>Shows increase of ζ with increasing T</td>
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<tr>
<td>Ishido and Mitzutani</td>
<td>1981</td>
<td>Flow through Streaming Potential</td>
<td>CC vs T, ζ vs T</td>
<td>Quartz, KNO₃, Al(NO₃)₃</td>
<td>20-75°C</td>
<td>Atm. Pressure</td>
<td>Developed empirical equations for ζ, ζ shown both an increase and decrease for increases in T</td>
</tr>
<tr>
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<td>1985</td>
<td>Streaming Potential</td>
<td>ζ vs T</td>
<td>SiO₂, Al₂O₃, NaCl, KCl, CaCl₂, K₂SO₄</td>
<td>20-250°C</td>
<td>7-8 MPa</td>
<td>Shows increase in ζ with increase of T</td>
</tr>
<tr>
<td>Morgan, Willaims, and Madden</td>
<td>1989</td>
<td>Flow through Streaming Potential</td>
<td>CC vs T, ζ vs T</td>
<td>Crushed Granite &amp; NaCl</td>
<td>5-70°C</td>
<td>Atm. Pressure</td>
<td>CC increased with increasing T, ζ remained constant with increasing T</td>
</tr>
<tr>
<td>Authors</td>
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<td>Measurement Technique</td>
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<td>Dunstan</td>
<td>1994</td>
<td>Electrophoresis</td>
<td>ζ vs T</td>
<td>Colloidal Silica, and KCl</td>
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</tr>
<tr>
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<td>1994</td>
<td>Streaming Potential</td>
<td></td>
<td>Polysulfone Membranes</td>
<td>20-70°C</td>
<td>Atm. Pressure</td>
<td>ζ does not show a temperature dependence</td>
</tr>
<tr>
<td>Pengra, Li and Wong</td>
<td>1999</td>
<td>Streaming Potential</td>
<td>CC</td>
<td>Fontainebleau Sandstone, Berea Sandstone, Glass Beads, Indiana Limestone in NaCl Brine</td>
<td>10-50°C</td>
<td>Atm. Pressure</td>
<td>Small increases in CC for Fontainebleau Sandstone and Glass Beads. Slight large increases for Berea Sandstone and Indiana Limestone</td>
</tr>
</tbody>
</table>
Figure 5.12 – Comparison of all the reported zeta potential data in this chapter. The asterisk in the legend represents measurements that were made using materials and solution chemistries similar to those found in the earth.
Figure 5.13 – Comparison of the zeta potential data in this chapter that used materials and solution chemistries similar to those found in the earth.
atmospheric pressure. As temperature is raised, possible outgassing of the water may affect results if sufficient pore pressure is not maintained. It also appears that all of the experimental systems except that of Pengra et al. used a flow-through apparatus with differing electrolytes. This allowed the concentration and pH of the samples to be maintained relatively constant with time and temperature. In summary there does not seem to be a clear pattern as to how streaming potential coupling coefficients or zeta potentials behave with changes of temperature. It might be said that the in many cases zeta potentials increase with temperature, but not for every case.

5.4 Temperature Dependence of Streaming Potential Coupling Coefficients

The temperature dependence of the Helmholtz-Smoluchowski equation will now be investigated by examining the temperature dependence of each of its parameters. The first parameter to be examined is the viscosity. The temperature dependence of viscosity has been extensively studied for water and is well understood [Atkins, 1982], and is given by

\[
\log \left( \frac{\eta_{20}}{\eta_T} \right) = \frac{1.37023([T/^\circ\text{C}] - 20) + 8.36 \times 10^{-4}([T/^\circ\text{C}] - 20)^2}{109 + [T/^\circ\text{C}]} \quad . \ (5.17)
\]

Where \( \eta_{20} \) is the viscosity at 20 \(^\circ\text{C} \) and \( T \) is the temperature. A plot of the temperature dependence of the viscosity of water is shown in Figure 5.14.
Figure 5.14 – Temperature dependent behavior of the viscosity of water.
The permittivity of water has a temperature dependence given by

\[ \varepsilon = \varepsilon_c + A(1 - T/T_c)^{-\alpha_c}, \]  

(5.18)
as presented by Fernandez et al. [1997], where A is a constant, \( \varepsilon_c \) is the permittivity at the critical point, \( T_c \) is the critical point temperature, \( T \) is the temperature, and \( \alpha_c \) is the critical exponent for the isochoric heat capacity. The temperature dependence of the permittivity of water has also been studied extensively, with a plot of the temperature dependence in Figure 5.15.

Conductivity is another parameter of the Helmholtz-Smoluchowski equation that has been studied extensively. The temperature dependence of the conductivity of a brine solution is

\[ \sigma(T) = \left(5.6 + 0.27T - 1.5 \times 10^{-4}T^2\right)M - \frac{2 + 0.099T}{1.0 + 0.114M}M^2, \]  

(5.19)
where \( T \) is the temperature and \( M \) is the molar concentration [Sen and Goode, 1992]. This empirical expression has good accuracy within the ranges of temperature and molar conductivity used in this chapter. The temperature dependence of a brine solution is given in Figure 5.16. The normalized temperature dependence of permittivity, viscosity, and conductivity is given in Figure 5.17, and the plot of \( \varepsilon/\eta\sigma \) is shown in Figure 5.18, which assumes a constant zeta potential. It can be seen in Figure 5.18 that the conductivity is the most dominant term in the temperature-dependent coupling coefficient equation.
Figure 5.15 – Temperature dependent behavior of the permittivity of water, where the relative dielectric constant is given.
Figure 5.16 – Temperature dependent behavior of brine solution of water.
Figure 5.17 – Comparison of the normalized viscosity, dielectric constant, and conductivity.
Figure 5.18 – Calculated coupling coefficient using the theoretical values for viscosity, permittivity, and conductivity. A constant zeta potential value was used.
5.5 Temperature Dependence of Zeta Potentials

In the previous section it was discussed that the Helmholtz-Smoluchowski equation, equation (5.11), cannot predict the temperature dependence of streaming potentials using the theoretical predictions for the variations of permittivity, viscosity, and conductivity with temperature and a constant zeta potential. The unpredictability is because the zeta potential can vary with temperature. This section examines some simple models for the temperature dependence of zeta potentials before investigating a more comprehensive model. In certain instances the simple models may be adequate for modeling zeta potentials under specific conditions.

The zeta potential (ζ) as shown by Hunter [1996], can be expressed as

$$\zeta = \varphi_d \exp(-\kappa \Delta_1)$$

(5.20)

which can be applicable for low potentials, as is often the situation with rocks. As can be seen in equation (5.20) the zeta potential is a function of the Stern plane potential, where \(\Delta_1\) is the distance that the slipping plane (zeta potential) is from the Stern plane, and \(\kappa\) is the Debye-Hückel parameter, sometimes referred to as the reciprocal double-layer thickness, given by

$$\kappa = \left(\frac{2e^2 I_f}{\varepsilon \kappa_B T}\right)^{\frac{1}{2}}$$

(5.21)
Where e is the charge of the electron, \( I_f \) is ionic strength of the fluid, \( k_B \) is the Boltzmann constant, \( \varepsilon \) is the permittivity of the fluid, and \( T \) is temperature in \(^\circ\)K. For some equilibrium conditions in the earth when the concentration term in equation (5.21) is less than 0.01 M, the zeta potential can be approximated by \( \varphi_d \) because the exponent of equation (5.20) can then be approximated by zero.

If the temperature dependence of equation (5.20) is examined by looking only at the temperature dependence of the Debye-Hückel parameter, the Debye-Hückel parameter cannot account for the zeta potential temperature dependence seen in the literature. For example, if a constant Stern-plane potential is assumed in equation (5.20), \( \Delta_l \) is assumed to be on the order of 10 angstroms [Hunter, 1981], and a fluid concentration of 0.001 M is used in equation (5.21), the temperature dependence of the zeta potential is found to be \(-1.235 \, \mu\text{V}/\text{C}^\circ\). A fluid concentration of 0.001 M is used in these calculations so that the results can be compared to the data of Ishido and Mizutani [1981] and Somasundaran and Kulkarni [1976] who used 0.001 M concentrations. Ishido and Mizutani (1983) measured a -0.33 mV/C\(^\circ\) increase, and Somasundaran and Kulkarni measured an increase of \(-1.0 \, \text{mV}/\text{C}^\circ\). It can be seen that the change in zeta potential due to the temperature dependence of the Debye-Hückel parameter is negligible compared to the results of Ishido and Mizutani and Somasundaran and Kulkarni. Zeta potentials calculated using the temperature-dependent Debye-Hückel parameter are compared to the data of Ishido and Mizutani and the data of Somasundaran and Kulkarni in Figure 5.19. For relatively weak electrolytes the zeta potential and the Stern-plane potential can be
Figure 5.19 – A comparison of the zeta potential values of Ishido & Mizutani and Somasundaran & Kulkarni to the calculated temperature dependent zeta potential values for: the temperature dependence of the Debye-Hückel (D-H) parameter on the zeta potential, and the temperature dependence of $\varphi_d$ on the zeta potential while assuming a constant surface charge, $\sigma_s$. 
considered the same [Overbeek, 1961; Revel, 1997]. For the purposes of this work, the zeta potential will be assumed to have the same value as $\varphi_d$ for the rest of this chapter unless otherwise noted.

The change in zeta potential due to temperature cannot be explained by the temperature dependence of the Debye-Hückel parameter. Therefore, alternative sources of the temperature dependence of zeta potentials must be explored. For the simplified Stern model of the electrical double layer (EDL) used in this chapter, where no charge exists between the Stern plane and the surface, the surface charge must be balanced by the charge in the diffuse layer, which gives

$$\sigma_o = \sigma_d \quad , \quad (5.22)$$

where $\sigma_o$ is the charge on the surface and $\sigma_d$ is the charge in the diffuse layer. An expression relating the surface charge to the diffuse layer potential, as given in many texts on colloid science [Hunter 1981; Lyklema, 1995] is

$$\sigma_o = \frac{2k_B T e}{z e} \sinh \left( \frac{-ze\varphi_d}{2k_B T} \right) \quad , \quad (5.23)$$

which can be also written as [Revil and Glover, 1997]

$$\sigma_o = \sqrt{8\varepsilon \varepsilon_0 k_B T N_A 10^3 (C_f + 10^{-pH} + 10^{pH-pK_a^{(T)}) \sinh \left( \frac{-ze\varphi_d}{2k_B T} \right)} \quad , \quad (5.24)$$
where $k_B$ is the Boltzmann constant, $z$ is the valence of the ion, $e$ is the charge of an electron, $\kappa$ is the reciprocal Debye length, $\varepsilon$ is the permittivity, $T$ is temperature in °K, $N_a$ is the Avogadro constant, $C_f$ is the ionic concentration of the fluid in m$^3$, $pK_w$ is the dissociation constant of water, and $\phi_d$ is the Stern plane potential. The parameters $\kappa$, $\varepsilon$, have a temperature dependence as shown in equations (5.18) and (5.21) respectively. The approximation that $\phi_d = \zeta$ is used, it is also assumed that the surface charge remains constant as the temperature changes. This approximation determines if the temperature dependence of the zeta potential is explained by the temperature dependence of the Stern-plane potential ($\phi_d$) on the surface charge ($\sigma_0$). The adjustable parameters in this approximation are $\kappa$ which uses a ionic concentration of 0.001 M in order to be compared to the data of Ishido and Mizutani [1981] and the data of Somasundaran and Kulkarni [1976]. The surface charge ($\sigma_0$) is adjusted to 4.9 mC/m$^2$ to give the same zeta potential at 25°C as the Ishido data. This approximation gives a temperature dependent increase in zeta potential of -0.3261 mV/°C, which does not equal the magnitude of Ishido’s or Somasundaran’s zeta potential increases as shown in Figure 5.19. It appears that the temperature dependence of $\phi_d$ can account for a significant part of the zeta potential change due to changes in temperature, however this zeta potential response to the temperature dependence of $\phi_d$ still does not explain the results for the limited data in the literature. Also, using this model, the slope of the zeta potential versus temperature plot cannot be varied. Therefore, further temperature-dependent mechanisms must be present. This points to the surface charge, which was assumed constant in the above approximations.
It should be noted as seen in Figure 5.20, where equation (5.24) is plotted for several different pH values, that the pKw temperature dependence has little to no importance at low to moderate pH values (<6). However, for pH values greater than six, the pKw temperature dependence can start to affect results.

Now that it has been determined that the temperature dependence of the surface charge must be used in calculating zeta potentials, the temperature dependence of the surface charge will be examined. The reaction at the quartz surface controlling the surface charge is given by

\[
K_{(\cdot)}^{(+)} \\
S - OH + H^+ \Leftrightarrow S - OH_2^+ 
\]  
(5.24)

\[
K_{(\cdot)}^{(-)} \\
S - OH \Leftrightarrow S - O^- + H^+ 
\]  
(5.26)

where S-OH represents surface hydroxyl groups and \( K_{(\cdot)}^{(+)} \) and \( K_{(\cdot)}^{(-)} \) are the equilibrium constants for the reactions.

For the relatively simple case of silica in a weak NaCl solution, where the potential determining ion is H\(^+\) [Parks, 1964; Davis et al., 1978], the surface charge density is given by

\[
\sigma_\gamma^0 = e\left(\Gamma_{sOH_2^+}^0 - \Gamma_{sO^-}^0\right) 
\]  
(5.27)
Figure 5.20 – The effect of the temperature dependence of pKw of water on the zeta potential using equation (5.24). Plots are shown for three different pH values for the background electrolyte. It can be seen that for a pH less the 6 the temperature dependence of pKw has no effect on the results. The concentration of the water is 0.001 M and the surface charge used is 0.05 C/m².
where $\Gamma_{\text{SiOH}_2}$ is the surface site density for SiOH$_2$ and $\Gamma_{\text{SiO}}$ is the surface site density for SiO'. Using mass balance equations, Revil and Glover [1997] have rewritten equation (5.28) as

$$
\sigma_s^0 = e\Gamma_s^0 \frac{1}{A} \left( K_{(\leftrightarrow)} C_{H^+}^0 - \frac{K_{(-)}}{C_{H^+}^0} \right)
$$

(5.29)

where $C_{H^+}$ is the concentration of hydrogen ions on the surface, $K_{(\leftrightarrow)}$ is the equilibrium constant for the reaction in equation (5.27), $K_{(\leftrightarrow)}$ is the equilibrium constant for the reaction in equation (5.26) and $\Gamma_s$ is the total surface concentration of ionic sites. The term $A$ is given by

$$
A = 1 + K_{(\leftrightarrow)} C_{H^+}^0 + \frac{K_{(-)}}{C_{H^+}^0} + K_{Na} \frac{C_{Na^+}^{f}}{C_{H^+}^{f}} + K_{Cl} C_{Cl}^{f} C_{Cl}^{f}.
$$

(5.30)

where $C_{H^+}^f$ is the concentration of hydrogen ions in the free electrolyte, $C_{Na}^{f}$ is the concentration of the Na ions in the electrolyte, $C_{Cl}^{f}$ is the concentration of Cl ions in the electrolyte, $K_{Na}$ is the equilibrium constant for the adsorption of Na ions on the surface and $K_{Cl}$ is the equilibrium constant for the adsorption of Cl ions on the surface. The surface charge can now be expressed as

$$
\sigma_s^0 = e\Gamma_s^0 \frac{K_{(\leftrightarrow)} C_{H^+}^0 - \frac{K_{(-)}}{C_{H^+}^0}}{1 + K_{(\leftrightarrow)} C_{H^+}^0 + \frac{K_{(-)}}{C_{H^+}^0} + K_{Na} \frac{C_{Na^+}^{f}}{C_{H^+}^{f}} + K_{Cl} C_{Cl}^{f} C_{Cl}^{f}}
$$

(5.31)

which is then substituted into
\[
\sigma_o = \sqrt{8e_f k_B T N_s} 10^3 (C_f + 10^{-pH} + 10^{pH-pK_w}) \sinh \left( \frac{-z \varepsilon \phi_d}{2k_B T} \right)
\] (5.32)

and solved for \(\phi_d\) where the equilibrium constants can be represented as

\[
K_{(\text{+})} = \frac{\{\text{SOH}^+\}}{\{\text{SOH}\}[\text{H}^+]} \quad \text{and} \quad K_{(-)} = \frac{\{\text{SO}^-\}}{\{\text{SOH}\}},
\] (5.33)

\[
K_{(\text{Na})} = \frac{\{\text{Na}^+\}}{\{\text{SOH}\}[\text{C}_{(\text{Na})}]} \quad \text{and} \quad K_{(\text{Cl})} = \frac{\text{Cl}^-}{[\text{H}^+][\text{SOH}][\text{C}_{(\text{Cl})}]},
\] (5.34)

where \{\} denotes the concentrations of surface species in moles per kilogram of absorbing solid, and [ ] represents the solution molar concentration in moles per liter. An appropriate handling of the temperature dependence of the equilibrium constant, as suggested by Hiemstra and van Riemsdijk [1989], would be to use the van't Hoff equation,

\[
\ln \left( \frac{K_T}{K_{T_0}} \right) = -\frac{\Delta H^0}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)
\] (5.35)

where \(\Delta H^0\) is the standard free enthalpy change of the reaction, \(K_{T_0}\) is the reference constant, \(K_T\) is the constant to be determined, \(R\) is the gas constant, \(T_0\) is the reference temperature in \(^o\text{K}\), and \(T\) is the new temperature in \(^o\text{K}\). The van't Hoff equation is valid as long as \(\Delta H^0\) is nearly constant in the temperature range being considered. If larger temperature variations are encountered, the variation of \(\Delta H^0\) should be determined for
that temperature range. \( \Delta H^o \) for quartz was found to have a large range of values that varied from 15kJ/mol to 90 kJ/mol [Berger et al., 1993; Hiemstra and van Riemsdijk, 1989; Bollis et al., 1991]. Values for \( K(\cdot) \) are found to vary from \( 10^{-5.7} \) to \( 10^{-9.8} \) [Bousse and Meindl, 1986; Hiemstra et al., 1989] where \( 10^{-9.8} \) is a theoretical upper limit that has not been seen experimentally.

Prior to examining the temperature dependence of the surface charge equations (5.31) and (5.32), values for the maximum number of surface sites available for the absorption of H\(^+\) ions must be found. The maximum number of surface sites available for adsorption does not appear to have a temperature dependence. However, it is difficult to obtain accurate values of surface site density for a specific specimen. The literature gives values for the surface site density ranging from 2.6 sites/nm\(^2\) to 15 sites/nm\(^2\) [Blum and Lasagna, 1988; Koretsky et al., 1998]. These values are found to vary with the crystal lattice that is exposed to the fluid.

Figure 5.21 shows the temperature dependence of the zeta potential using equation (5.32) with the temperature dependence of the surface charge included. The assumption is made that the concentration of H\(^+\) ions in the free electrolyte equals the concentration of H\(^+\) ions on the surface, in equation (5.31), and they remain constant with changes in temperature. This is may not be a valid assumption but it is useful in understanding the contribution of the temperature dependence of surface charge to the temperature dependence of the zeta potential. In this solution of equation (5.32) shown in Figure 5.21 the values used for the parameters in equation (5.30) are \( \Gamma_s^0 = 2 \) sites/nm\(^2\), \( K(\cdot) \)
Figure 5.21 – A comparison of the data of Ishido & Mizutani and Somasundaran & Kulkarni to the approximated surface charge temperature dependent model of equation (5.27). Three pH values are shown, pH 6 is the pH of the data. The other two pH values (pH4, pH 8) show the sensitivity of the model to pH.
= 10^{-7}, K_{(+)} = 10^{-13}, \text{pH} = 6, C_{\text{Cl}} = 10^{-3} \text{ M}, C_{\text{Na}} = 10^{-3} \text{ M}, K_{\text{Na}} = 10^{-7}, K_{\text{Cl}} = 10^{-6}, \Delta H_{(+)} = -8 \text{ kJ/mol}, \Delta H_{\text{Na}} = -20 \text{ kJ/mol}. \ Two\ other\ plots\ are\ shown\ in\ Figure\ 5.21,\ where\ the\ pH\ of\ 4\ and\ 8\ are\ also\ used\ to\ plot\ the\ zeta\ potential\ with\ all\ other\ parameters\ remain\ the\ same.\ These\ plots\ show\ that\ the\ model\ is\ very\ sensitive\ to\ pH.\ The\ potential\ determining\ reactions\ are\ the\ de-adsorption\ of\ H^+\ and\ Na^+\ from\ the\ surface.\ The\ plot\ of\ zeta\ potential\ versus\ temperature\ using\ the\ temperature\ dependence\ of\ surface\ charge,\ equation\ (5.32)\ shows\ a\ good\ correlation\ with\ the\ data\ of\ Ishido\ and\ Mizutani\ [1981]\ and\ Somasundaran\ and\ Kulkarni\ [1973].\ It\ was\ found\ that\ the\ slope\ of\ this\ curve\ is\ controlled\ by\ \Delta H.\ The\ magnitude\ of\ the\ zeta\ potential\ at\ room\ temperature\ is\ controlled\ primarily\ by\ the\ surface\ site\ density\ and\ secondarily\ by\ the\ equilibrium\ constant\ K.\ Although\ there\ is\ a\ good\ fit\ of\ the\ theory\ to\ the\ data\ using\ this\ approximation,\ it\ cannot\ be\ said\ that\ the\ model\ is\ accurate.\ This\ is\ because\ the\ true\ values\ for\ the\ adjustable\ parameters,\ is\ unknown.\ Therefore,\ it\ can\ be\ said\ that\ the\ model\ gives\ correct\ trends,\ but\ the\ accuracy\ of\ the\ model\ is\ suspect\ because\ the\ values\ for\ the\ adjustable\ parameters\ required\ to\ fit\ the\ data\ are\ not\ in\ the\ normal\ range\ of\ the\ parameters.

Using a Maxwell-Boltzmann distribution [Landau and Lifshitz, 1980] for the ionic concentration in the electrical double layer, $C_{\text{H}^+}^o$ can be rewritten as

$$
C_{\text{H}^+}^o = C_{\text{H}^+}^f \exp \left( \frac{-e\phi_d}{k_B T} \right),
$$

(5.36)

consequently the surface charge can be represented below, as given by Revil and Glover [1997],
\[ \sigma^* = \frac{e\Gamma^*}{\sigma^*} \frac{K_{(+)C_{H^+}} \exp(-e\varphi_d/k_B T) - K_{(-)} \exp(e\varphi_d/k_B T)}{1 + \frac{K_{(+)C_{H^+}}}{\exp(e\varphi_d/k_B T)} + \frac{K_{(-)}}{C_{H^+} \exp(-e\varphi_d/k_B T)} + K_{Na} \frac{C_{Na}^{f}}{C_{H^+}^{f}} + K_{Cl} \frac{C_{Cl}^{f}}{C_{H^+}^{f}}} \cdot (5.37) \]

In equation (5.37) the surface charge has an explicit temperature dependence in \( T \).

Equation (5.37) also has a temperature dependence due to the equilibrium constants \( K \) and the potential \( \varphi_d \).

In their 1997 zeta potential solution, Revil and Glover do a nonlinear solution of equation (5.37) combined with equation (5.32). Their formulation requires that the \( \varphi_d \) satisfy the electroneutrality requirement between the surface charge density and the diffuse-layer charge density in equilibrium conditions, as shown in equation (5.22). An exact analytical solution to this problem does not exist but an approximate solution does exist. To determine \( \varphi_d \), Revil and Glover [1997] set the surface charge, determined based on surface chemistry reactions, equation (5.37) equal to the charge in the diffuse layer.

The diffuse layer charge density can be expressed as

\[ \sigma_d = \sqrt{8\varepsilon_f(T)k_B T N_A 10^3(C_f + 10^{-pHF} + 10^{pH-pK_w(T)}) \sinh\left(\frac{-e\varphi_d}{2k_B T}\right))}. \quad (5.38) \]

They solve this problem by combining equations (5.37) and (5.38) and calling the combined function \( F(X) \). Electroneutrality requires that \( F(X) = 0 \) where \( F(X) \),

\[ F(X) = \frac{n}{2} \sqrt{C_f + 10^{-pHF} + 10^{pH-pK_w(T)}} \left(X - \frac{1}{X}\right) \left(1 + K_{(+)10^{-pHF}X^2} + \frac{K_{(-)}}{10^{-pHF}} X^{-2} + \frac{K_{(Na)}^{C_{Na}^{f}} + K_{(Cl)}^{C_{Cl}^{f}} 10^{-pHF}}{10^{-pHF} X^{-2} - K_{(-)}^{10^{-pHF}} X^{-2} = 0} \right) \quad (5.39) \]
and

\[ X \equiv \exp\left(\frac{-e\phi_d}{k_B T}/2\right) \quad , \quad (5.40) \]

and

\[ n = \frac{\sqrt{8e_f(T)k_B TN_\Lambda}10^3}{e\Gamma^o_s} \quad . \quad (5.41) \]

where \( C_f \) is the concentration of the bulk electrolyte in the fluid in m\(^{-3}\). The solution of equation (5.39) is achieved numerically by solving for the roots of \( X \). Neglecting second-order and higher-order effects and making the assumption that the \( H^+ \) and \( OH^- \) are the potential-determining ions in weak electrolyte solutions [Parks, 1964; Davis et al., 1978], equation (5.39) can be simplified to

\[ F(X, T) = \frac{n(T)}{2} \sqrt{C_f + 10^{-pH + 10^{pH-pK_s(T)}}} \left( X - \frac{1}{X} \right) \left( 1 + \frac{1}{K_{(\cdot)}(T)} 10^{-pH} X^2 \right) - 1 \quad (5.42) \]

with the temperature dependence also shown, [Reppert and Morgan, 1999; Morgan, 1999]. In their 1997 paper, Revil and Glover solve for the zeta potential but do not address temperature effects in their paper.
Now that all of the parameters are defined, one can solve for $X$ in equation (5.39) and ultimately the Stern-plane potential ($\varphi_d$), which approximates the zeta potential. Equation (5.40) can be rewritten to give the Stern-plane potential in terms of $X$,

$$\varphi_d = \frac{k_B T \ln(2X)}{-e}$$

(5.43)

Therefore, the $\varphi_d$ and thus the zeta potential can be determined for each temperature after $X$ is determined at each temperature.

A limited check of the model of Revil and Glover [1997] to predict the temperature dependence of streaming potentials is demonstrated. The model is fitted to the data of Somasundaran and Kulkarni [1973] [Figure 5.22], and to the data of Ishido and Mizutani [1981] also in Figure 5.22. The model results were calculated using the low and high range of $\Gamma^0_s$ [Blum and Lasagna, 1988; Koretsky et al., 1998] and $K_\epsilon$ [Bousse and Meindl, 1986; Hiemstra et al., 1989] found in the literature for 25°C. An enthalpy of 40 kJ/mol [Berger et al., 1993; Hiemstra and van Riemsdijk, 1989; Bollis et al., 1991] is used in the van't Hoff equation, equation (5.31), to estimate the temperature dependence of $K_\epsilon$. It can be seen that the data from both Somasundaran and Kulkarni [1973] and Ishido and Mizutani [1981] fall within the ranges predicted by the model extremes of Revil and Glover [1997]. The best-fit model parameters for the Somasundaran and Kulkarni data give a $\Delta H^\circ$ of -30 kJ/mol, $\Gamma^0_s$ of 4.5 sites/nm$^2$, and a $K_\epsilon$ of $10^{-7.0}$, and the best fit to Ishido and Mizutani data gives a $\Delta H^\circ$ of -20 kJ/mol, $\Gamma^0_s$ of 4.6 sites/nm$^2$, and a $K_\epsilon$ of $10^{-7.3}$. The pH and concentration used to fit both data sets were
Figure 5.22 – A comparison of the data of Ishido & Mizutani and Somasundaran & Kulkarni to the temperature dependent Revil and Glover [1997] model results, assuming that H⁺ and OH⁻ are the potential determining ions of the system. Also shown are the high and low limits of the model using the extreme range of the model parameters found in the literature.
Figure 5.23 – A comparison of the Revil and Glover model to the data of Alekhin et al., [1984]. These results indicate the model can accommodate variations in pH.
pH = 6 and a concentration of 10^{-3} M. As another test of the Revil and Glover model, it is compared Figure 5.23 to the data of Alekhin et al., [1984] which was collected with a pH of 4. The data of Alekhin et al., was collected over a temperature range of 25-200 °C in solution of 10^{-3} NaCl. Because it is a weak electrolyte [Parks, 1965] and because it has been shown that Na^+ does not absorb onto quartz at low pH [Berger et. al., 1993] the simplified model is used. The parameters used to fit the data are a ΔH^o of -10 kJ/mol, Γ^o_s of 5.5 sites/nm^2, and a K(\gamma) of 10^{-6.3}

Lastly, a comparison of the approximated solution for zeta potentials, using the approximated temperature dependent surface charge model to the Revil and Glover non-linear solution is made in Figure 5.24. In Figure 5.24 both models have the same input parameters as those in Figure 5.22. It appears that the approximated solution overestimates that amount of charge on the surface by a factor of 3-5. Based on this observation, the inclusion by Revil and Glover of the Maxwell-Boltzmann distribution of ions within the electrical double layer appears to give a more complete solution. Also, the values used for the adjustable parameters in the Revil and Glover model are more in-line with expected values. This can be better understood by looking Figure 5.25a, where equation (5.36) is plotted versus temperature for different zeta potential values. It can be seen by looking at Figure 5.25b, that the ratio of C^o to C^o is on the order of 3-5 for a 10^{-3} M solution and a zeta potential of 60 mV. Which, is agreement with the results seen in Figure 5.24.
Figure 5.24 – A comparison of the data of Ishido & to the temperature dependent Revil and Glover [1997] model results, and to the approximated surface charge temperature dependent model of equation (5.27). The two models are using the same parameters as used in the Ishido model of Figure 5.22.
Figure 5.25  – a) A comparison of the H⁺ concentrations found at the surface is made using equation (5.36) and different zeta potential values. b) The ratio of the H⁺ concentration at the surface to the concentration in the bulk fluid is shown. The pH in the bulk fluid is 6.
5.6 Conclusion

A review of the temperature dependence of streaming potential coupling coefficients and zeta potentials has been conducted. Because the literature has a wide range of materials and solution compositions for which the temperature dependence of the zeta potential and the coupling coefficient were measured, no simple clear picture emerges. It has been concluded however, that if the temperature dependence of the zeta potential can be predicted, then the behavior of the coupling coefficient can also be predicted. It does appear that zeta potentials do increase in magnitude with temperature in most cases. Also, as part of the chapter, the theory of streaming potentials has been presented with an emphasis on the temperature dependence of the streaming potential coupling coefficient. The temperature dependence of the permittivity, conductivity, and viscosity has been adequately addressed in prior literature. It has been determined that the temperature dependence of the zeta potential is controlled primarily by the temperature dependence of the surface charge. The temperature dependence of the surface charge appears to be controlled by surface site density, pH, and the intrinsic dissociation constant. Future research in this area will be required to determine if the surface site density, pH, or the intrinsic dissociation constant, are second-order effects.
5.7 References


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Chapter 6

Temperature Dependent Streaming Potentials
(Measurement and Interpretation)

6.1 Introduction

With the renewed interest in using streaming potentials to monitor flow in geothermal regions [Revil et al., 1999], a knowledge of the temperature dependence of streaming potentials is required. Several authors have attempted to measure streaming potentials at elevated temperatures, the highest temperatures being Alekhin et al., [1984] and Jayaweera et al., [1994], but none have attempted reaching true equilibrium conditions. Chapter 5 presents a more thorough treatment of previous work on streaming
potentials at elevated temperature. A new method for making measurements of equilibrium streaming potential coupling coefficients at elevated temperature is demonstrated in this paper.

One reason for studying streaming potentials at elevated temperature is to use the results in realistic modeling of streaming potentials in the earth. Knowledge of equilibrium streaming potentials at in situ conditions is required for realistic modeling. The uses range from modeling groundwater flow to modeling flow in geothermal regions [Fitterman and Corwin, 1982; Sill, 1983, Ishido et al., 1984]. Another reason for understanding how streaming potential coupling coefficients respond to temperature is that it may help scientists understand the processes that generate electromagnetic events associated with earthquakes. There are several hypothesis as to the mechanisms causing these electromagnetic events, ranging from streaming potential related phenomena [Morgan, 1995], to piezoelectric phenomena [Parrot, 1995].

Measurement of streaming potentials at elevated temperature and at equilibrium conditions is difficult. Most authors have attempted to make elevated-temperature measurements at atmospheric pressure in order to avoid the difficulties of measuring streaming potentials in a pressure vessel. However, this approach does not allow for significant temperature variation if outgassing of the water is to be avoided. Some of the problems associated with measuring streaming potentials at elevated temperature include electrical isolation of the sample and degradation of the electrodes. Electrodes used for long periods of time at elevated temperature experience degradation. This can adversely
affect measurements of DC streaming potentials. Also, when doing measurements in a pressure vessel, electrical isolation of the sample from the pressure vessel and steel pore-fluid tubing can be difficult. Solutions to these problems are presented in this paper.

Two investigators have attempted to measure streaming potential coupling coefficients at elevated temperature in pressure vessels [Jayaweera et al., 1994, Alekhin et al., 1984]. Neither investigator used intact rocks: Jayaweera [1994] used powered oxides in a flow-through apparatus with platinum electrodes, and Alekhin [1984] used powered SiO₂ and Al₂O₃ samples in a flow-through apparatus with platinum electrodes. The use of platinum electrodes in DC streaming potential experiments has been shown by Korpi and DeBruyn [1971] and Morgan et al., [1989] to give errors due to polarization effects. Polarization can occur when using non-reversible electrodes. The investigators listed above were not able to obtain in situ conditions using their flow-through apparatus. This is because they did not change the fluid after each temperature change to ensure that the fluid was at equilibrium with the rock for both the dissolution and adsorption processes.

This chapter presents the first measurements of equilibrium streaming potential coupling coefficients on intact rocks at elevated temperature and pressure. The experimental apparatus is presented first, followed by the experimental methodology. Lastly, data on coupling coefficients and zeta potentials are presented for three intact rocks at temperatures ranging from 23°C to 200°C. The model presented in the
companion paper [Reppert and Morgan, 2000] is fitted to the data as a preliminary verification of the model.

6.2 Experimental System

The experimental system used in these experiments was originally the permeameter used by Bernarbe [1987]. This experimental system was intended to perform transient permeability tests at constant temperature. The rig was modified by installing a New England Research (NER) pressure vessel and heating it with Watlow bandheaters. The temperature of the confining fluid inside the pressure vessel was controlled using a Watlow temperature controller and SRC. Using this temperature control system, the maximum temperature was restricted to temperatures lower than 204°C because of the oil and 238°C because of the O-rings. Therefore, the maximum temperature was constrained to be about 200°C. The permeameter schematic is shown in Figure 6.1. It consists of a pressure vessel with a confining pressure circuit, which is controlled by a pressure-control valve not shown in the figure. The pore-fluid system has both an absolute pressure transducer and a differential pressure transducer monitoring the pore fluid pressure. In the figure there are two fluid reservoirs, denoted as reservoirs 1 and 2, and an accumulator. The fluid inside the sample was oscillated by controlling the volume inside reservoir 2 using valve E.

Several modifications had to be made to the pore-fluid part of the permeameter in order to use the permeameter for these streaming potential measurements. The tubing
Low-T Permeameter

1. Pore-Fluid System (@ Temperature)

Figure 6.1 - Schematic diagram of the pressure vessel and associated control systems, similar to that used by Bernarbe, [1987].
in the pore-fluid part is stainless steel, which electrically shorts out both sides of the sample. Figure 6.2 shows a simplified pore-fluid part of the circuit including the stainless steel plug. The stainless steel plug holds the sample in the pressure vessel, and also acts as a short circuit to both sides of the sample. In order to perform these experiments, both sides of the sample must be electrically isolated. This task is further complicated by the fact that both the tubing and the pore fluid can conduct electricity. The electrical isolation was achieved in two steps. First, a new plug was constructed (Figure 6.3) using a fluid feed through device that electrical isolates the fluid, which was provided by NER and constructed by Kemlon corporation. This device allows the pore fluid to pass through the plug while remaining electrically isolated from the plug. The second step was to isolate the pore fluid from the rest of the permeameter tubing. This was achieved by constructing a second isolation device that electrically isolated the fluid in the sample from the rest of the fluid in the pore-fluid system while allowing pressure to be transmitted through the device. This isolation device consists of two pieces of 316 stainless steel with pore fluid connections and a cavity in each half of the device. The two halves are bolted together with an O-ring and a thin piece of silicon rubber in between the two halves to provide the electrical isolation while letting the pressure pass through the device. The new plug and fluid isolation devices combine to form the modified electrically isolated pore-fluid system shown in Figure 6.4.

The next problem to overcome was getting the electrodes into the pore-fluid system. This is problematic because the sample is encased in a material that keeps the confining fluid out of the sample. When trying to get any wire through this casing, there
Figure 6.2- The original pore fluid system which allowed the two ends of the sample to be short circuited through the SST tubing.
Feed-thru tubing must not contact plug

SST Plug

Isolated feed-thru device

O-ring

Holes drilled for feed-thru device

Figure 6.3 - Modified plug design containing the isolated fluid feed through devices.
Figure 6.4 - Modified pore fluid system which isolates the fluid from the rest of the pore fluid system as well as electrically isolates the rock sample form the pressure vessel tubing.
is a risk of having confining fluid wick along the wire into the sample. This problem was solved in two different ways, which gave equivalent results. One solution was to install an electrode in the side of the endplug (Figure 6.5). Because of size limitations, however it was not possible to keep the electrode out of the fluid path in the endplug. Also, when filling the system with fluid, it is not known whether any air gets trapped near the electrode. The other method was to use the endplugs as electrodes because they were electrically isolated and trapped air would not be an issue in end plugs without holes drilled in them for electrodes. Because the streaming potentials were being measured using the sinusoidal method as described in Appendix A, and by Reppert and Morgan [2000], the electrodes did not have to be reversible electrodes, which was verified by experiments not shown in the thesis. This allowed the end plugs to be used as electrodes.

In order to get the pore fluid to oscillate, valve E on reservoir 2 was manually opened and closed to give a sinusoidal signal of approximately 0.5 Hz. This sinusoidal pressure signal was reproducible and gave consistent results. Throughout the experiment, the pore-fluid pressure was maintained at 50 bars and the confining fluid pressure was maintained at 200 bars. In order for water not boil at 200 °C the confining pressure has to be greater than 15.5 bar [Kuzman and Raznjevic, 1995]. Consequently, at 200 bar confining pressure, the experimental confining pressure was sufficient to prevent outgassing.

The data were collected using a 16 bit A/D converter with the following inputs: confining-fluid pressure, pore-fluid pressure, differential pressure, and the electrode
Figure 6.5 - Modified end plug. Plug was modified to accept an electrode into the pore fluid system.
signals. The data were stored for later processing. Data were collected periodically as the rock and solution came to equilibrium. The conductance of the sample was measured each time streaming potential data were collected.

**Summary of Improvements/Modifications Made to Pressure-Vessel System**

- Provided a means to electrically isolate the rock sample from the fluid in the rest of the pore-fluid system
- Devised a system to get two sets of electrodes next to the rock sample in order to monitor streaming potentials
- A consistent, accurate means for collecting the data was devised which allowed the fluid to remain in the rock, i.e., the flow-through methods could not be used.
- A new plug for the pressure vessel was designed and constructed that isolated the pore fluid from the plug.

### 6.3 Methodology for Measurement of Conductivity

Conductivity measurements were made in order to convert streaming potential coupling coefficients to zeta potentials as well as determine solution concentration for later use in the model. To accomplish this, the conductances of the samples were measured using a conductivity meter. The conductance was measured at the beginning and end of each measurement and then converted to rock conductivity, $\sigma_{\text{rock}}$, using the dimensions of the sample. The Berea sandstone sample initially contained di-ionized water, and the Fontainebleau sandstone and Westerly Granite samples initially contained 0.001M NaCl.
The conductivity data at the lower temperatures was extrapolated to infinite time using a least-squares method, ensuring that equilibrium values were obtained for the conductivity. The extrapolated values are the final values used in the zeta potential calculations. At the higher temperatures, the conductance changed too rapidly to capture enough of the curve to extrapolate. In these instances the system was considered to be at pseudo equilibrium when there was less than a 5% change in the results over a 12 hour period.

Formation Factor measurements were needed as an essential part of this experiment to determine the pore-fluid conductivity and concentration. The pore-fluid system is a closed system in which the rock is dissolving, and continually changing the pore-fluid conductivity. Therefore, the only way to determine the pore fluid conductivity is by making measurements of the rock conductivity and converting them to pore-fluid conductivity through the use of Formation Factor information on the rocks.

Formation Factor measurements were made in the laboratory on the rock samples at room temperature and atmospheric pressure by measuring the rock conductivity and the conductivity of the pore fluid. A plot of rock conductivity versus water conductivity for the various rock samples is shown in Figure 6.6. This plot was used to convert the rock conductivity of the samples in the pressure vessel to pore-fluid conductivity. The Formation Factor (F) of the rock is

\[
\sigma_{\text{rock}} = \frac{\sigma_r}{F}, \quad (6.1)
\]
Figure 6.6 - Water conductivity plotted versus rock conductivity for the Berea sample and the Fontainebleau sample.
Figure 6.7 - Formation factor plotted versus rock conductivity for the Fontainebleau and Berea samples.
where $\sigma_{\text{rock}}$ is the conductivity of the rock and fluid and $\sigma_f$ is the conductivity of the fluid. Figure 6.7 shows the formation factor versus rock conductivity for the Fontainebleau Sandstone and Berea Sandstone samples. The formation factor can also be expressed using Archie's Law [Archie, 1942] where the formation factor is given as a function of the rock porosity as shown in equation (6.2):

$$\frac{1}{F} = \phi^{-m}$$  \hspace{1cm} (6.2)

$\phi$ is the porosity of the sample and $m$ is a constant that is approximately 2 for the majority of sandstones (Guéguen and Palciauskas, 1994) and is approximately 1.87 for Berea Sandstone. The Berea Sandstone formation factor at high solution concentrations was determined using Figure 6.7 to be 20.5. Using Equation (6.2) and the formation factor at high concentrations, a porosity of 20.7% was determined for the Berea Sandstone, which is in good agreement with the measured porosity of 19.9% for the Berea Sandstone sample. The porosity of the Fontainebleau Sandstone and Westerly Granite samples was measured and found to be 30% and 0.3%, respectively. The porosity value for the Westerly Granite is in good agreement with values given by Brace [1978]. The calculated formation factors for Fontainebleau Sandstone and Westerly Granite are 32 and 1150 respectively. The calculated formation factor for Berea sandstone is in agreement with the finding of Yale [1984]. Yale also conducted formation factor experiments at different confining pressures. For Berea Sandstone, Yale found roughly a 6% change in formation factor between measurements at atmospheric pressure and those at 200 bars. The samples in these experiments had 200 bars confining pressure. Therefore, although the formation factor measurements do not directly correspond to the
pressure conditions in the experiment, they are sufficient to give the correct trend of the corrected data.

6.4 Conductivity Data

The samples conductance was measured each time a coupling coefficient data point was collected. The conductance was then converted to a rock conductivity using the dimensions of the sample. Using the formation factor information on the rock, the solution conductivity and conductance was then obtained. Figure 6.8 shows representative data on rock conductivity. These data were collected on the Berea Sandstone sample at 60°C. Using a least-squares method, a curve was fitted to the data using the function \( A + B \exp(-Ct) \) where \( A \), \( B \), and \( C \) are constants. The curve was then extrapolated to infinite time. The extrapolated curve for the Berea Sandstone sample is shown in Figure 6.8 as the solid line.

The extrapolated/final values of rock conductivity for all temperatures measured are shown in Figure 6.9. These conductivity values were then used in future equilibrium calculations of zeta potential and for the calculation of the fluid concentration for use in the model. The room temperature conductivity and coupling coefficient measurements were made in a different apparatus than the rest of the measurements. This might explain why the room temperature conductivity measurements seem to be out lying points compared to the rest of the data. The other apparatus was not under pressure and may not have reached a value close to equilibrium due to the larger volume of water in the container. It is expected that all three curves should have similar trends in the
Figure 6.8 - Berea conductivity data at 40°C shown with the extrapolated conductivity values. Extrapolated values were determined using a least squares approach.
Figure 6.9 - Rock Conductivity plotted versus temperature for the Fontainebleau, Berea, and Westerly samples.
conductivity versus temperature behavior but they should have different magnitudes as seen. Figure 6.10 shows calculated water conductivity for Fontainebleau Sandstone versus temperature compared to the temperature dependent conductivity of brine water given by

$$\sigma(T) = \left(5.6 + 0.27T - 1.5 \times 10^{-4}T^2\right)M - \frac{2. + 0.099T}{1.0 + 0.114M} M^{\frac{3}{2}},$$

(6.3)

where $T$ is the temperature and $M$ is the molar concentration of the water. It can be seen that the conductivity of the Fontainebleau water increased significantly compared to the theoretical prediction for brine water. This is expected due to the dissolution of the rock.

### 6.5 Streaming Potential Coupling Coefficient Measurements

The streaming potential measurements were collected using the oscillatory method as outlined in Appendix A. Figure 6.11 is a sample of the raw data collected, with the streaming potential signal shown as the dotted line and the differential pressure as the solid line. It can be seen in this figure that the streaming potential and differential pressure signals are 180 degrees out of phase. This $180^\circ$ phase difference indicates a negative streaming potential cross-coupling coefficient.

Fourier analysis was applied to both the streaming potential and differential-pressure signals in Figure 6.11, with typical results shown in Figure 6.12. The frequency of the signals is 0.4 Hz, as can be seen by the location of the peaks in Figure 6.12. The ratio of the streaming potential response in Figure 6.12b to the differential pressure response of Figure 6.12b is calculated, which gives the cross coupling response of Figure
Figure 6.10 – Solution conductivity plotted versus temperature for the Fontainebleau Sandstone sample plotted along with the theoretical conductivity versus temperature curve.
Figure 6.11 - Sample of the raw data collected in the pressure vessel using the sinusoidal driving source.
Figure 6.12 - a) Representative frequency response for the pressure signal. b) Representative frequency response for the streaming potential signal. The frequency for the driving source was at .4 Hz.
6.13. For a more thorough explanation of this procedure, please refer to Appendix A. At frequencies other than the measurement/driving frequency, the signal to noise ratio can be poor thus causing large errors in the coupling coefficient calculations, as is evident at 0.9 Hz in Figure 6.13. This procedure was done for each measurement at each temperature. The results of the 23°C Fontainebleau Sandstone measurements are shown in Figure 6.14 with the data extrapolated to infinite time. The extrapolation was accomplished using a least-squares approach. The extrapolated/final values for the coupling coefficient were then used in the calculations for the zeta potential. Again, as with the conductivity data, at the higher temperatures the coupling coefficient changes too rapidly to capture the data for extrapolation purposes. In these cases when the coupling coefficient changed by less than 5% over a 12 hour period the system was considered to be at pseudo equilibrium.

Figures 6.15, 6.16, and 6.17 show the time histories for all the coupling-coefficient measurements along with the extrapolated values for the Fontainebleau Sandstone, Berea Sandstone and Westerly Granite samples, respectively. As can be seen in these figure it takes considerable time for equilibrium conditions to be reached. Only the final equilibrium values are shown in Figure 6.18.

It can be seen in Figure 6.18 that the behavior of the coupling coefficient is not the same for the three samples. The coupling coefficient for the Berea Sandstone sample decreases until 160°C, at which point it starts to increase. The Fontainebleau Sandstone sample has a behavior similar to the Berea Sandstone sample but after it turns around it
Figure 6.13 - Representative coupling coefficient response where the pressure signal of Figure 6.11a was divided into the streaming potential response of Figure 6.11b.
Figure 6.14 - Time history of coupling coefficient measurements at 23°C for the Fontainebleau sample. The solid line shows the extrapolated values.
Figure 6.15 - Time and temperature history of all Fontainebleau Sandstone coupling coefficient measurements. The time at each temperature is the initial time at that temperature and the final time of the previous temperature.
Figure 6.16 - Time and temperature history of all Berea Sandstone coupling coefficient measurements. The initial time is shown for each temperature which is also the final time for the previous temperature. The 25°C measurement only has the final time shown.
Figure 6.17 - Time and temperature history of all Westerly Granite coupling coefficient measurements. The initial time is shown for each temperature which is also the final time for the previous temperature.
Figure 6.18 - Equilibrium coupling coefficient measurements versus temperature for Fontainebleau Sandstone, Berea Sandstone, and Westerly Granite.
does not increase as rapidly. The Westerly Granite sample has a behavior completely different than the Fontainebleau Sandstone or Berea Sandstone samples. Its coupling coefficient increases with temperature until 120°C, where it then decreases until it reaches 160°C, where it increases again. The behavior of the temperature-dependent coupling-coefficient for Westerly Granite may be different because Westerly Granite has a very different petrology than the Fontainebleau Sandstone and Berea Sandstone samples. Table 1 lists the Westerly Granite petrology, Table 2 lists the Berea Sandstone petrology, and the Fontainebleau Sandstone petrology is 99% quartz.

The zeta potential and the adjusted zeta potential were then calculated for each measurement of the coupling coefficient. The adjusted zeta potential was corrected for surface conductance using

\[
CC_{\text{corrected}} = \frac{\text{r}_C}{F_{\text{Sol}}} CC
\]  

(6.3)

This correction multiplies the coupling coefficient by the ratio of the formation factor at high concentration (F_\text{r}) to the formation factor measured at the concentration of the solution (F_{\text{Sol}}). The measured formation factors at various solution concentrations are given in section 6.2. The zeta potentials for the Fontainebleau Sandstone, Berea Sandstone, and Westerly Granite samples are shown in Figures 6.19, 6.20, and 6.21, respectively, with all three corrected zeta potentials shown in Figure 6.22. In these figures, two zeta potentials are shown; one is for the uncorrected data and the second is corrected for surface conduction. It is difficult to draw comparisons to any previous data because these are the first experiments where the pH and concentration were allowed to
<table>
<thead>
<tr>
<th>Mineral</th>
<th>% Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plagioclase</td>
<td>38%</td>
</tr>
<tr>
<td>Quartz</td>
<td>29%</td>
</tr>
<tr>
<td>Feldspar</td>
<td>26%</td>
</tr>
<tr>
<td>Biotite</td>
<td>3.8%</td>
</tr>
<tr>
<td>Muscovites</td>
<td>1.4%</td>
</tr>
<tr>
<td>Chlorite</td>
<td>0.8%</td>
</tr>
<tr>
<td>Apatite, Ilmenite, Hematite, Titanite</td>
<td>Trace</td>
</tr>
</tbody>
</table>

Rutter and Neumann [1995]

Table 6.1) – Petrology for Westerly Granite
<table>
<thead>
<tr>
<th>Mineral</th>
<th>% Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>53%</td>
</tr>
<tr>
<td>Chert</td>
<td>2%</td>
</tr>
<tr>
<td>Feldspar</td>
<td>3%</td>
</tr>
<tr>
<td>Carbonate</td>
<td>0%</td>
</tr>
<tr>
<td>Lithics</td>
<td>8%</td>
</tr>
<tr>
<td>Opaques</td>
<td>Trace</td>
</tr>
<tr>
<td><strong>Cement Matrix</strong></td>
<td><strong>Quartz Overgrowth – 11%</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Clay – 6%</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Carbonate – 7%</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Chlorite – 1%</strong></td>
</tr>
</tbody>
</table>

Table 6.2) – Petrographic description of Berea Sandstone from Yale [1984].
Figure 6.19 - Fontainebleau Sandstone zeta potentials versus temperature. Values are shown for zeta potentials corrected for surface conduction and for zeta potentials not corrected for surface conductance.
Figure 6.20 - Berea Sandstone zeta potentials versus temperature. Values are shown for zeta potentials corrected for surface conduction and for zeta potentials not corrected for surface conductance.
Figure 6.21 - Westerly Granite zeta potentials versus temperature. Values are shown for zeta potentials corrected for surface conduction and for zeta potentials not corrected for surface conductance.
Figure 6.22 – Comparison of all zeta potentials
vary. However, some very basic trends might be compared, such as the data of Alekhin et al., [1984] were the Alumina data shows a decrease in zeta potential with temperature. Also the silica sample shows some similarity to the Fontainebleau sample in this work.

The zeta potential for both the Fontainebleau Sandstone and Berea Sandstone samples increase with temperature. Also, for both samples the zeta potential appears to have two different slopes. The change in slope for the Fontainebleau Sandstone sample appears to occur around 120°C, and the change in slope for the Berea Sandstone sample appears to occur around 160°C. Because the zeta potential is determined by the interfacial chemistry, it appears that something is changing in the chemistry to cause the slope change. The zeta potentials for the Westerly Granite sample have an even more complicated temperature dependent behavior. It is possible that behavior is in part due to the feldspar present in the granite as well as the other constituents in the granite besides the quartz.

The Fontainebleau Sandstone sample has the simplest chemistry of the three samples, consisting of NaCl, H₂O, and quartz. It should be noted that other substances appear to be in the Fontainebleau Sandstone sample because at room temperature the pH was measured at 8.3. A quartz-water system as mentioned above should be acidic and not basic. Also, the water sample collected after the 200°C measurement shows other constituents in the water (Table 6.3), besides water and silicon. It is possible that some of these contaminants were adsorbed onto the quartz surface and thus reducing the surface charge of the quartz which may be evident in the lower than expected zeta potential.
<table>
<thead>
<tr>
<th>Species</th>
<th>$200^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.5</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.1</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>0.08</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>$&lt;0.05$</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>$&lt;0.5$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>1.8</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>9.9</td>
</tr>
<tr>
<td>K$^+$</td>
<td>5.3</td>
</tr>
</tbody>
</table>

Table 6.3 – List of dissolved species in mg/l of water in contact with Fontainebleau Sandstone at equilibrium, for the temperatures of $200^\circ$C.
reading for the Fontainebleau sample. As the temperature increased these contaminants (some of which were multivalent ions as shown in Table 6.3) were released from the surface which may help explain the change in slope at the higher temperatures. Here are two more possible explanations for the change in slope of the Fontainebleau Sandstone sample. Sverjensky et al. [1997] present data and a model that show the temperature dependence of the equilibrium constant (pK) for

$$\text{SiO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SiO}_3^- + \text{H}^+ \quad \text{(6.4)}$$

which decreases in value from 25°C to approximately 150°C, at which point it starts to increase. This implies that if the solubility of the SiO\(_2\) remains constant the pH decreases during the initial part of the experiment and when the temperature gets above 150°C the pH starts to increase. When the pH is decreasing, smaller zeta potentials are observed as the point of zero charge (PZC) is approached. The PZC for quartz has been reported to be 2.3 by Parks [1964]. Also, Berger et al. [1993] show a pH dependence for the adsorption of Na\(^+\) on quartz for two temperatures. It can be deduced from their data that when the pH drops below 6, and less adsorption of Na\(^+\) occurs on the surface. It is not known however whether the pH was below 6 during the experiment. The pH measurement of 5.5 at the end of the experiment indicates that the pH could have been below 6. There are a range of values for how the equilibrium constant changes with temperature for this system [Busey and Mesmer, 1977], and consequently the exact pH at elevated temperatures cannot be known. The pH measurement was made after the sample had cooled down to approximately 40-50°C.
Another possible reason for the change in slope has to do with impurities in the system. A water sample collected at the end of the experiment, after the sample had cooled from 200°C, showed other substances such as Fe$^{2+}$, Al$^{3+}$ in the water besides quartz and NaCl (Table 6.3). It is also possible that some of the other substances found in the solution affected the streaming potential measurements. Some of these impurities might be due to dissolution of the stainless steel in the pore-fluid system.

The Berea sandstone sample has a more complicated composition, as shown in Table 6.4, which lists the chemical speciation of Berea Sandstone as given by Pettijohn et al. [1972]. Table 6.5 shows the chemical speciation at several temperatures for different water samples taken from a Berea Sandstone sample, which was in a batch reactor. In the case of the Berea Sandstone several different ions are available for adsorption that compete with H$^+$ for adsorption sites, so that ions leaving the surface as the temperature increases will have several different dissociation constants governing their behavior. Because the Berea Sandstone has a moderate quartz content, the arguments used for the Fontainebleau Sandstone are applied to the Berea Sandstone sample. The Berea Sandstone also contains kaolinite, which can dissolve at temperatures greater than 80°C and be completely dissolved at 160°C as reported by Milliken et al. [1981]. In the temperature range of the Berea Sandstone slope change, therefore at least two possible chemistry changes occurring, one associated with the kaolinite and the other associated with the desorption of the larger ions from the surface. At room temperature, the Berea Sandstone sample had a measured pH of 8.3, which is much higher than expected. Similar results were obtained by Shaw et al. [1989], who postulated that the higher pH
<table>
<thead>
<tr>
<th>Mineralogy</th>
<th>Leverett and Van Horn (1931)</th>
<th>Eakins (1890)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>93.13</td>
<td>92.91</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.86</td>
<td>3.78</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.11</td>
<td>Trace</td>
</tr>
<tr>
<td>FeO</td>
<td>0.54</td>
<td>0.91</td>
</tr>
<tr>
<td>MgO</td>
<td>0.25</td>
<td>Trace</td>
</tr>
<tr>
<td>CaO</td>
<td>0.19</td>
<td>0.31</td>
</tr>
<tr>
<td>Na₂O</td>
<td></td>
<td>0.34</td>
</tr>
<tr>
<td>K₂O</td>
<td></td>
<td>0.61</td>
</tr>
<tr>
<td>H₂O⁺</td>
<td></td>
<td>1.19</td>
</tr>
<tr>
<td>H₂O⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ign. loss</td>
<td>1.43</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>99.51</td>
<td>100.05</td>
</tr>
</tbody>
</table>

*Pettijohn et al., [1972]*

Table 6.4) – Mineralogy for Berea Sandstone from two different sources found in Pettijohn, Potter, and Siever, 1972.
<table>
<thead>
<tr>
<th>Species</th>
<th>25°C</th>
<th>40°C</th>
<th>60°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>2.3</td>
<td>2.7</td>
<td>8.2</td>
<td>20.2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>4.9</td>
<td>5.8</td>
<td>17.5</td>
<td>43.5</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>0.09</td>
<td>0.05</td>
<td>0.05</td>
<td>0.08</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td></td>
<td></td>
<td>0.1413</td>
<td>0.1</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>17.1</td>
<td>13.6</td>
<td>15.6</td>
<td>10.6</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>53.3</td>
<td>47.1</td>
<td>38.8</td>
<td>47.9</td>
</tr>
<tr>
<td>Na⁺</td>
<td>17</td>
<td>11.6</td>
<td>11.7</td>
<td>18.5</td>
</tr>
<tr>
<td>K⁺</td>
<td>8.8</td>
<td>150</td>
<td>68.8</td>
<td>200</td>
</tr>
</tbody>
</table>

Table 6.5 – List of dissolved species in mg/l of water in contact with Berea Sandstone at equilibrium, for the temperatures of 25°C, 40°C, 60°C and 80°C.
was due to bicarbonate left in the rock from groundwater at the quarry. The pH of the sample fluid was not obtained at the end of the experiment, because of contamination of the sample when removing it from the pressure vessel. Lastly, the same pH-induced slope changes suggested for the Fontainebleau Sandstone sample may also apply to the Berea Sandstone sample. This can be inferred because pH measurements in batch reactors show the pH decreasing with increasing temperature.

The Westerly Granite sample has an even more complicated behavior of the temperature-dependent zeta potential (Figure 6.20). With the complicated petrology of the Westerly Granite (Table 6.1), it is pure speculation as to what is happening at the rock-fluid interfaces. Behavior of the zeta potential versus temperature must be obtained for each individual component of the Westerly before trying to make any inferences about the behavior of the sample as a whole. The pH of the sample fluid was not obtained at the end of the experiment, because of contamination of the sample when removing it from the pressure vessel.

6.6 Bench-top Measurements

Attempts were made at measuring pH in batch reactors to get pH measurements for later use in modeling. It was discovered, however that the pH measurements were unreliable, for several reasons. One reason is that the pH measurements were being made in a system that was open to the atmosphere which allowed CO₂ gas to enter the system, unlike in the pressure vessel. Also, pH probes are not designed to operate at temperatures above 90°C; thus the water had to be cooled to temperatures below 90°C before
measuring pH. It was observed that the pH changed rapidly during cooling. It was concluded that this was possibly due to the temperature still decreasing during the measurement as well as the fact that the solutions were not buffered. It was also observed that the pH probe had to be in the solution for several minutes to get a stable reading, even in a buffered solution. Consequently, reliable pH measurements could not be obtained. A subsequent approach was considered, by which the pH of the fluid next to the rock sample was measured after it was removed from the pressure vessel. An estimate of the pH at 200°C would then be made using the van’t Hoff equation to estimate the equilibrium constant and consequently the pH at the end of the experiment. This method was rejected because over the temperature range of interest the $\Delta H^0$ in the van’t Hoff equation can vary enough to affect results. Another approach was to use the equilibrium-constant data from Sverjensky et al. [1996] and Busey and Mesmer [1977] and recalculate the pH. After closer examination, however, there was too much variation in the equilibrium-constant data for an accurate final pH at 200°C to be obtained. Also Si concentrations in the fluid are unknown which makes calculation of pH unreliable. The approach finally used to obtain pH values for use in the modeling was to use the initial room-temperature pH measurement and the measurement after the sample was removed from the vessel and still warm (60-70 °C) . Table 6.6. Although these measurements may not have an accurate pH value, due to little buffering in the solution, they do give a general trend as to what the pH is for the sample. A straight line was then interpolated between the two pH measurements. The errors using this method are comparable to the other methods. At this stage of modeling, however, interpolation of the pH gives the correct trend, which is sufficient for the present purposes of the modeling.
<table>
<thead>
<tr>
<th>Time of Measurement</th>
<th>Fontainebleau Sandstone</th>
<th>Berea Sandstone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beginning of Experiment</td>
<td>8.1</td>
<td>8.3</td>
</tr>
<tr>
<td>End of Experiment</td>
<td>5.5</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 6.6 – pH measurements at the beginning of the experiment and at the end of the experiment for Fontainebleau and Berea Sandstone.
Water samples from batch reactors containing Fontainebleau and Berea Sandstone samples at different temperatures, were sent to a laboratory for analysis. The purpose of this analysis was to get some quantitative idea about the solution speciation. A list of the measured chemical speciation for the Fontainebleau Sandstone sample is given in Table 6.2, where the Fontainebleau Sandstone is 99% quartz. Table 6.5 shows the measured composition for the water in contact with the Berea Sandstone and Tables 6.2 and 6.4 list the petrology and mineralogy of the Berea Sandstone from Yale [1984] and Pettijohn [1972].

6.7 Comparison of Data with the Model

The data from the Fontainebleau and Berea Sandstone samples are here compared with the modified model of Revil and Glover [1997], presented in chapter 5 and which is re-shown in Equation (6.4). The Westerly Granite data is not compared to the model because of the complex chemistry of Westerly Granite of which quartz is not a majority constituent of. The present time the model is based on quartz and water comprising the dominant chemical reaction.

\[
F(X, T) = \frac{n(T)}{2} \sqrt{C_f + 10^{-pH} + 10^{pH-pK_w(T)}} \left( X - \frac{1}{X} \right) \left( 1 + \frac{1}{K_-(T)} 10^{-pH} X^2 \right) - 1 , \quad (6.4)
\]

where

\[
n(T) = \sqrt{8\epsilon_f(T)k_nTN_A 10^{-3}} \quad \frac{e\Gamma_5^o}{}, \quad (6.5)
\]

and \( C_f \) is the ionic concentration of the fluid, and
\[ K_{(-)} = \frac{[SO^-][H^+]}{[SOH]} \]  \hspace{1cm} (6.6)

To initially compare the experimental results with the model, several assumptions are made. The first assumption is that the zeta potential or surface potential is controlled by the hydroxide ion, and that the salts play a minor role in the adsorption process on quartz (Parks, 1964; Davis et al., 1977). This assumption is valid as long as the solution is not concentrated. Next, we make the assumption of a simple system consisting only of quartz and water (for the purposes of surface complexation). This gives the reaction shown in equation (6.7):

\[ \text{SiOH} \leftrightarrow \text{SiO}^- + \text{H}^+ \]  \hspace{1cm} (6.7)

Again it should be noted that the Berea Sandstone has a more complicated petrology than just quartz, as can be seen in Table 6.2. Because the major constituent of the Berea Sandstone is quartz, 58 percent (Yale 1984), both the Fontainebleau and Berea Sandstone models will use the intrinsic surface complexation constant for quartz and also the surface site density for quartz. Lastly, we assume that \( \Delta H^0 \) of the reaction in equation (6.7) remains constant over the temperature range of interest, which is not a completely valid approximation but is assumed because the variation of \( \Delta H^0 \) with temperature is unknown.

The parameters calculated for the salt concentration and estimated for the pH over the temperature range measured are input into the model, with the model results shown in Figure 6.23 and Figure 6.24 for the Fontainebleau and Berea Sandstone samples,
Figure 6.23 - Comparison of Fontainebleau Sandstone corrected zeta potentials to the best fit model. The adjustable model parameters are $K_0 = 6$, $\Gamma_0 = 4.5$ sites/nm$^2$ and $\Delta H = 60,000$ J/mol.
Figure 6.24 - Comparison of Fontainebleau Sandstone corrected zeta potentials to the best fit model. The adjustable model parameters are $K_{(e)} = 7.8$, $\Gamma_0 = 5$ site/nm$^2$ and $\Delta H = 50,000$ J/mol.
respectively. Table 6.7 list the parameters used in the model and shows how they were obtained. There are ten parameters to the model listed in Table 6.7, of which only three are adjustable in the model and one is estimated, the intrinsic dissociation constant, surface site density and $\Delta H^0$ are adjustable and the pH is estimated. The model results show the same trend as in the data prior to the change in slope. It was also found that the simple model could not fit the data using realistic values for the surface site density and the dissociation constant. The model gave zeta potentials larger than the values in the data. When Na$^+$ was included in the complete model as originally shown in equation (5.35) of the previous chapter and re-shown below,

$$F(X) = \frac{n}{2} \sqrt{C_f + 10^{-pH} + 10^{pH-pK_w}} \left( X - \frac{1}{X} \right) \left( 1 + K_{(+)} 10^{-pH} X^2 + \frac{K_{(-)}}{10^{-pH}} X^{-2} \right) + \frac{K_{(Na)}}{10^{-pH}} C_{Na} + K_{(Cl)} C_{(Cl)} 10^{-pH} + K_{(-)} 10^{-pH} X^2 - \frac{K_{(-)}}{10^{-pH}} X^{-2} = 0 \quad (6.8)$$

the zeta potentials of the model were lowered. The adjustable parameters used in the model fitted to the Fontainebleau Sandstone sample are $K_{(c)} = 6$, $\Gamma_o = 4.5$ sites/nm$^2$ and $\Delta H^0 = 60,000$ J/mol. The adjustable parameters used in the model fit to the Berea Sandstone sample are $K_{(c)} = 7.8$, $\Gamma_o = 5$ site/nm$^2$ and $\Delta H^0 = 50,000$ J/mol. It was also observed while fitting the model to the data that $\Delta H$ controlled the slope of the zeta potential, whereas the primary effect of $K_{(c)}$ and $\Gamma_o$ is to change the magnitude of the zeta potential versus temperature. If the pH and the other model parameters are known, complete verification of the temperature dependence of the model can be achieved. If any of the parameters are unknown, only the general trend can be established. It should
<table>
<thead>
<tr>
<th>Input Parameter</th>
<th>Method Obtained</th>
</tr>
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<tbody>
<tr>
<td>Dielectric Constant</td>
<td>Theory</td>
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<tr>
<td>C&lt;sub&gt;r&lt;/sub&gt; Solution Concentration</td>
<td>Measured</td>
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<td>Temperature</td>
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<td>pH</td>
<td>Estimated based on measurements</td>
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<tr>
<td>pK&lt;sub&gt;w&lt;/sub&gt;</td>
<td>CRC Chemistry and Physics</td>
</tr>
<tr>
<td>*ΔH</td>
<td>Adjusted between 15 and 90kJ/mol, Berger et al., [1993]; Hiemstra et al, [1989a,b]; Bollis et al., [1991]</td>
</tr>
<tr>
<td>δ</td>
<td>Calculated from pH&lt;sub&gt;prn&lt;/sub&gt;</td>
</tr>
<tr>
<td>Δ&lt;sub&gt;I&lt;/sub&gt;</td>
<td>Estimated from the literature</td>
</tr>
<tr>
<td></td>
<td>Ishido and Mizutani [1981], Revil and Glover [1997]</td>
</tr>
<tr>
<td>*Γ&lt;sup&gt;s&lt;/sup&gt;</td>
<td>Adjusted between 2.6 and 15 sites/nm&lt;sup&gt;2&lt;/sup&gt;, Blum &amp; Lasagna [1988], Koretsky et al., [1988]</td>
</tr>
<tr>
<td>*pK&lt;sub&gt;(+)&lt;/sub&gt;</td>
<td>Adjusted between −5.7 and −9.8, Bousse and Meindl, [1986]; Hiemstra et al., [1989]</td>
</tr>
</tbody>
</table>

Table 6.7 – Model input parameters for the zeta potential versus temperature model. The parameters with an * are parameters that were adjusted in the model in order to fit the model to the data. Parameters without an * were fixed based on a priori information.
be noted that the model is not smooth because actual fluid concentrations were used in the model, which give the model curve the irregular shape.

6.8 Future Work

As seen in the applications section there are a wide variety of possible uses for streaming potential coupling coefficients at elevated temperature. However, it must be reiterated that the ability to model streaming potentials in the earth is based on having realistic values for the coupling coefficient. Therefore, the immediate future work should be aimed at determining realistic values for a wider range of materials. The results in this paper also show promise for predicting the temperature-dependent behavior of the zeta potential using models. Experiments must now be developed to obtain the thermodynamic parameters for quartz and other minerals. To accomplish this, experiments need to be conducted where the surface site density and the equilibrium constant are the only unknowns. To accomplish this requires that pH be measured in situ.

Some of the specific tasks for the future include

- Do more elevated temperature measurements on a wider range of rock types.
- Do more elevated temperature tests on wide range mono-mineral samples in order to understand the behavior of the individual components of more complicated rocks
- Constructing a zirconium pH probe that can be used at elevated temperature and pressures for future tests.
- Determining thermodynamic parameters for quartz in NaCl and KCl by conducting tests in which the pH remains constant and only the concentration of the solution is
varied by known amounts. This test should be repeated at several different
temperatures.

6.9 Conclusion

A pressure vessel was modified to measure equilibrium streaming potentials at
elevated temperatures and pressures. Measurements of coupling coefficients showed a
decrease as the temperature increased for Fontainebleau and Berea Sandstones until
approximately 140°C was reached, at which time they both started to increase. The
experiments showed that the coupling coefficient for Westerly granite increased then
decreased and then increased with increasing temperature. For the Fontainebleau and
Berea Sandstone samples the zeta potential increased with increasing temperature. The
Zeta potential for Westerly Granite decreased with temperature until 150°C, where it then
started to increase. The Zeta potentials for both the Fontainebleau and Berea Sandstone
samples show a change in slope as the temperature is increased. This change of slope
might be related to the behavior of the acid-base equilibrium constants and/or the
competition for surface sites between H⁺ ions and larger ions in the solution. It is also
possible that this slope change is related to influences of the experimental system.
Further experimentation is required to verify if the slope change is real or an artifact of
the experimental system.
6.10 References


Hiemstra, T., J.C.M. De Wit, and W. H. Van Riemsdijk, Multisite Proton Adsorption Modeling at the solid/solution interface of (Hydr) oxides; A new approach – II Application to various important (Hydr) oxides, *J. Colloid Interface Sci.*, 133, 1, 105-116, 1989b.


Chapter 7

Applications of Temperature-Dependent Streaming Potentials

7.1 Introduction

It is too early in this research on temperature-dependent streaming potentials to make any definitive statements concerning the ramifications of this research, but several possible applications show promise for future use in geophysics. This chapter will discuss some of the possible applications related to temperature-dependent streaming potentials
7.2 Hydrogeological Flow

As mentioned earlier in this chapter, inverse modeling of hydrogeological flow from self-potential measurements may provide quantitative information about subsurface flow by using surface measurements. The most generalized expression hydrodynamic and electrical flows is [de Groot and Mazur, 1962]

\[ j = -L_{11} \nabla \phi - L_{12} \nabla P \]  
(7.1)

\[ q = -L_{21} \nabla \phi - L_{22} \nabla P \]  
(7.2)

Where \( j \) is the electrical current density, \( q \) is the volume flow density, \( \nabla \phi \) is the electrical potential gradient, \( \nabla P \) is the pore pressure gradient, \( L_{12} \) and \( L_{21} \) are the phenomenological coefficients. The first term in equation (6.9) represents Ohm’s law and the \( L_{12} \) term represents the cross-coupling coefficient. In equation (6.10) \( L_{21} \) represents the cross-coupling coefficient and the second terms represents Darcy’s law. According to Onsagers reciprocal relations \( L_{12} = L_{21} \), [de Groot and Mazur, 1962]. It can be seen that there is a direct relationship between the electrical current density and the volume flow density, which has been explored by others, [Ishido and Mizutani, 1981; Sill, 1983; Fitterman and Corwin, 1982, Wurmstich and Morgan, 1994]. It is this relationship that makes it possible to obtain fluid flow information from streaming potential measurements. Essentially what these equations say, is that if the current source at depth can be determined through inverse modeling, using streaming potential data and
resistivity data, the pressure gradient at depth can be determined. However, this is based on having realistic values for streaming potential coupling coefficients at *in situ* conditions. Once the pressure gradient is determined, a subsurface flow can be estimated based on the estimated permeability of the formation. Having realistic values for the *in situ* coupling coefficient can greatly reduce possible errors incurred during the inversion for underground fluid flow. This methodology can be applied to a variety of flow problems ranging from flow in aquifers to flow in geothermal regions.

### 7.3 Earthquake Prediction and Monitoring

As mentioned in chapter 5, scientists have been examining streaming potentials as a possible source of electromagnetic events associated with earthquakes [Mizutani et al., 1976; Ishido et al., 1981; Morgan et al., 1989; Parrot, 1995]. In his 1989 paper, Morgan reviews previous literature [Nur, 1972; Nur and Booker, 1972; Scholz et al., 1973; Mizutani et al., 1976; Corwin and Morrison, 1977] that suggests a dilatant zone in the area of an imminent earthquake may induce flow inward toward the zone, thus producing a positive streaming potential anomaly. A 90mV anomaly was recorded in California by Corwin and Morrison [1977] who argued that the anomaly could be caused by flow towards the dilatant zone if a streaming potential coupling coefficient of 1.3 μV/Pa is assumed. As seen in the section 6.5 of this chapter, coupling coefficients on the order of 0.1 μV/Pa were measured, which are much lower than what Corwin and Morrison predicted. It should also be pointed out that at temperatures above 293 °C the conductivity starts to decrease with increasing temperature [xxxx]. The depth at which the temperature reaches 293°C is roughly around 15km, which is near the bottom of the
seismogenic zone. Therefore, it is not likely that a change in conductivity contributed to the values measured by Corwin and Morrison.

Both Ishido and Mizutani [1981] and Morgan et al. [1989] discuss the expected magnitudes of streaming potentials measured at the surface due to earthquake induced water movement. In both papers the values for in situ coupling coefficients are estimated based on low temperature coupling coefficient values. This research can provide realistic values for streaming potential coupling coefficients to be used in future modeling aimed at determining if electromagnetic events associated with earthquakes are related to streaming potentials. This research shows that H⁺ ions tend to leave the surface at elevated temperatures thus allowing the surface to have higher surface charges. Once realistic values for the water chemistry in the seismogenic is known, it will be possible to determine what realistic coupling coefficients are in these regions. The data of this research indicates that the coupling coefficient will not be large.

Mizutani et al. [1976] suggest that a strong electromagnetic field may be used to generate electroosmotic flow and thus alter the subsurface flow and reduce the pore pressure in the dilatant zone. Consequently, it is suggested that some control may be maintained over and imminent earthquake.

This research also gives preliminary evidence that can be used by researchers who are studying electromagnetic events associated with the actual earthquake and not the possible flow induced prior to an earthquake. The experiments of this thesis indicate that
for quartz surfaces the zeta potential and consequently the surface charge increases with temperature up to 200°C. This implies that there may be significant charge available for causing the electromagnetic events. Future experiments are required to establish trends at higher temperatures and also to determine the electrokinetic properties of other minerals.

The experiments of this thesis suggest a means for understanding how H⁺ ions can enter quartz and cause chemical weakening. Kronenberg [1994] discusses how fluid inclusions and H⁺ ions in quartz can cause weakening of quartz. Using the model proposed by Morgan [1995], in which a pore space under tectonic stresses can close down and rapidly squeeze out the pore fluid, creating a streaming current that can be detected on the earth’s surface. It is plausible that this phenomenon would leave a charge imbalance where the pore surface was located, prior to the pore closing. The magnitude of the charge imbalance is governed by the number of H⁺ ions left on the surface, which is controlled by interfacial chemistry. It can be seen that understanding the interfacial chemistry of rocks at in situ conditions will help us to determine if weakening of quartz induced by H⁺ ions can be occurring in the seismogenic zone.

7.4 Resistivity of the Earth’s Crust

Another reason for studying streaming potentials at elevated and temperature is that it may be useful for understanding the resistivity of the crust. The resistivity of the crust has been of interest to earth scientist for many years [Brace, 1971; Olhoeft, 1981; Shankland and Ander, 1983; Haak and Hutton, 1986; Jones, 1992; Nesbitt, 1993]. In
general, it has been shown that the resistivity of the crust decreases with increasing depth [Nesbitt, 1993]. Explanations for this behavior range from fluid inclusions, serpentinites, graphite, partial melts and magnetic oxides and sulfides [Nesbitt, 1993]. By understanding streaming potentials at elevated temperature and pressure, insight into the temperature dependent behavior of the electrical double layer can be obtained. The electrical double layer can contribute significantly to the surface conductivity of rocks [Revil and Glover, 1997]. Research concerning streaming potentials at elevated temperature may help to answer the question; is surface conductance a major contributor to the reduced resistivity of the lower crust. The research completed to date on streaming potentials at elevated temperature indicates that the surface charge increases with increasing temperature. Temperature-dependent streaming potential data may imply that the surface conductance may also be increasing with increasing temperature. Examining the maximum number of surface sites on quartz we find the maximum charge that can exist on a quartz surface if 0.416-2.4 C/m, for 2.6-15 surface sites/nm² [Blum and Lasagna, 1988; Koretsky et al., 1998]. This represents a significant number of ions in the EDL that can contribute to surface conduction.

7.5 In Situ pH Measurements

Lastly, a possible use of streaming potentials at elevated temperature is related to the pH dependence of zeta potentials. If the model of Revil and Glover [1997] can be verified over a wide range of conditions, the dependence of the zeta potential on pH might be used to measure pH at in situ conditions. Currently there are no ways of
measuring pH inside a pore space, and methods for measuring pH at elevated temperature and pressure are very limited. If a quartz capillary whose thermodynamic parameters have been determined is used, the capillary can be placed in a fluid flow path and the coupling coefficient measured. From the coupling coefficient and the zeta potential the pH can be determined. It should be noted that the chemical composition of the water is also required to accomplish this task. As for the in situ pH measurements, currently there is no method for measuring the true pH in rocks at depth. If a rock and water sample are obtained from a borehole, the thermodynamic parameters for that sample and the chemical composition of the water can be determined and used to evaluate the in situ coupling coefficient measurement. Consequently, if either the in situ temperature or the pH are known the other parameter can be determined from streaming potential measurements. Therefore, streaming potentials at elevated temperature could possibly be used as either a pH or a temperature indicator.

7.6 Conclusion

Although there are many potential applications for temperature-dependent streaming potentials, present-day research has not gotten to the point where these applications can be in place in the immediate future. This points to the need for more research in both the understanding of temperature-dependent streaming potentials as well as in the areas in which it can be applied. However, it must be emphasized that recent advances have been made, of which this research has contributed, that will make utilization of temperature-dependent streaming potentials a reality in the future.
7.7 References


Chapter 8

Summary/Conclusion

8.1 Introduction

This thesis has covered a broad range of topics in the field of electrokinetics, ranging from frequency-dependent streaming potentials to frequency-dependent electroomosis and finally to streaming potentials at elevated temperature and pressure. The primary emphasis of the thesis has been to better understand the fundamental nature of these phenomena in order to utilize them in the earth sciences. Discussions of potential future applications of these phenomena have also been presented.
8.2 Frequency-Dependent Streaming Potentials

For the first time, the real and imaginary components of the streaming potentials coupling coefficients were measures. Also for the first time, data on frequency-dependent streaming potentials for porous media agreed with the theory. These data pushed the frequency range out to where inertial effects started to dominate over viscous effects. It was also verified that the frequency behavior of porous media is determined by the pore radius due to hydraulic effects within the pore space. Consequently, rock permeability has the potential for being determined using this method.

8.3 Frequency-Dependent Electroosmosis

The frequency behavior of the electroosmosis coupling coefficient is examined for the first time. The first analytical expression for the frequency-dependent electroosmosis coupling coefficient was derived. The electroosmosis coupling coefficient has a behavior similar to, but not identical to, that of the streaming potential coupling coefficient. The difference in behavior between the two phenomena is related to differences in the fluid velocity profiles caused by the initial driving force. The theory and analytical expression is confirmed using data collected on a 0.127 mm capillary, where the agreement between theory and data is excellent. Frequency-dependent electroosmosis has a potential use for determining the permeability of rocks. A possible advantage over frequency-dependent streaming potentials is its ability to measure the electroosmotic pressure at high frequencies.
8.4 Streaming Potentials at Elevated Temperature and Pressure

A review of streaming potentials measurements at elevated temperature is made, along with a presentation of the theory for streaming potentials at elevated temperature. It is determined that that the temperature dependence of all the parameters required to calculate the streaming potential coupling coefficient are well known except the zeta potential. Data on streaming potential coupling-coefficient were collected on Berea Sandstone, Fontainebleau Sandstone, and Westerly Granite between 23°C and 200°C. These are the first measurements of equilibrium coupling-coefficient attempting to simulate in situ conditions. The coupling-coefficient data shows a strong dependence on the conductivity of the sample. The zeta potentials for the three samples all show a general trend to increase with increasing temperature. Lastly, the zeta potential data for the Fontainebleau Sandstone and Berea Sandstone are compared with a model presented in the theory. The model results show the same trend as the data for low to intermediate temperatures but does not show the change of slope found in the data at higher temperatures.

These experiments demonstrate an effective methodology for making measurements of streaming potential coupling-coefficient at simulated in situ conditions. The experiments also show which parameters need to be tightly controlled in future experiments aimed at verifying the temperature dependence of the zeta potential model.
Appendix A

Collecting and Processing DC, AC, and Transient Streaming Potentials

A.1 Introduction

When preparing to make measurements of streaming potential coupling coefficients it is important to know which measurement technique and data-processing scheme is best suited to a specific application. In recent years, there have been advances in acquisition and processing streaming potential data, but there has not been any comprehensive comparison of the different methods.
In 1952, Packard (1) presented a method for measuring AC streaming potentials and the associated coupling coefficients as a function of frequency and also as a function of pressure. Packard processed his AC data using the RMS methodology. In 1973, Somasundaran and Kulkarni (2) presented a new apparatus for measuring DC streaming potentials which automated data collection and allowed measurements to be done at elevated temperatures. They analyzed the data to determine coupling coefficients using the traditional method, which is to determine the slope of the data in the streaming potential versus pressure plots. In 1971, Korpi and DeBruyn (3) analyzed the effects of electrode polarization on measurements of DC streaming potential and determined that silver silver-chloride electrodes have advantages over platinum electrodes. In 1975 and 1978, Sears and Groves (4, 5) presented modifications to Packard’s experimental apparatus for collecting streaming potential measurements as a function of frequency and pressure. Their data were analyzed using the RMS method. Alekhin et.al. (6) and Jayaweera et al. (7) in 1985 and 1994 respectively, presented an approach for measuring high-temperature DC streaming potentials up to 200°C. In 1995, Jouniaux and Pozzi (8) used transient and DC methods for measuring streaming potentials under triaxial stress. They did not describe how they processed their transient data. They also reported discrepancies between their transient results and their DC results. In 1995, Pengra et. al. (9) developed an apparatus and data-acquisition technique for measuring low frequency streaming potentials. They used a phase lock loop amplifier and digital signal analyzer to look at the signals. In 1998 and 2000, Reppert et al. (10, 11) developed a new apparatus for measuring wide bandwidth AC streaming potentials. This methodology made use of spectrum analysis to look at the real and imaginary parts of the signal. Also in 1999,
Reppert and Morgan (12) presented a new method for acquiring streaming potential data while simulating earth in situ conditions of elevated temperatures and pressures. This work showed that using the AC technique or transient allowed the pore fluids to remain in the sample during the testing until equilibrium conditions were reached.

As can be seen from the recent literature, most advances in streaming potential measurements have been to the experimental apparatus. Little information in the literature has been given concerning the collection and processing techniques associated with streaming potentials. Consequently, it is not always apparent which data-collection or data-processing technique is best suited for one's experiment. There are three basic methods for collecting streaming potential data; DC, AC, and transient. There are also five basic methods presented for processing and analyzing the data: filtering DC data, RMS, cross-correlation, spectral analysis, and using the raw data. It is the intent of this study to make a comparison of the different collection methods and processing techniques of streaming potential coupling coefficient data. The DC case is presented first, followed by the AC case and then by the transient data processing and collection techniques.

A.2 DC Streaming Potentials

DC streaming potentials have been extensively studied for over 100 years with numerous treatments of the subject in a variety of journals. It is not the intent of this section to give a detailed treatment of streaming potentials, but rather to give a brief review for the reader who is not acquainted with the subject. For a detailed treatment of
the subject, please refer to texts in colloid science such as those by Hunter (13) and Lyklema (14).

Streaming potentials occur in a fluid when there is relative motion between the fluid and a charged surface. At the interface between the fluid and the charged surface an electrical double layer (EDL) forms. This double layer has a charge density that decays exponentially away from the surface. The distance at which this charge density decays by 1/e is referred to as the Debye length. The Debye length can extend from a few nanometers for a concentrated electrolyte solution to a few hundred nanometers for a dilute electrolyte solution. As the fluid moves tangentially to the double layer it pulls the ions of the double layer along. These moving ions near the surface give rise to a convection current,

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

where \( v(r) \) is the fluid velocity and \( \rho(r) \) is the charge density. Evaluating the integral and applying the appropriate boundary conditions gives

\[ I_{\text{conv}} = \frac{\pi \varepsilon a^2 \zeta \Delta P}{\eta l} \quad , \]

where \( \eta \) is the viscosity of the fluid, \( \varepsilon \) is the permittivity of the fluid, \( a \) is the radius of the capillary or pore, and \( \zeta \) is the zeta potential, which is the potential at the slipping plane. The slipping plane is the plane where the fluid velocity goes to zero. From equilibrium considerations, a conduction current forms in the bulk of the fluid to balance the convection current near the surface. The conduction current,
\[ I_{\text{cond}} = \frac{\pi \sigma a^2}{l} \Delta V, \quad [A3] \]

flows through the resistive bulk fluid to generate a potential referred to as the streaming potential. \( \Delta V \) is the voltage measured across the sample, and \( \sigma \) is the conductivity of the fluid. Setting the convection current equal to the conduction current gives rise to the Helmholtz-Smoluchowski equation,

\[ \Delta V = \frac{\varepsilon \xi}{\eta \sigma} \Delta P, \quad [A4] \]

where \( \Delta V/\Delta P \) is referred to as the coupling coefficient.

### A.3 DC Collection and Processing Techniques

Flow-through streaming potentials are created when a constant differential pressure is applied across the sample, inducing a constant flow through the sample. The differential pressure and voltage across the sample are measured and are repeated for several different pressures, with a plot of the raw data shown in Figure A1. The resulting voltages are then plotted versus the differential pressures, as shown in Figure A2. The slope of the best-fit line through the data is the coupling coefficient, mV/Pa. It should be noted that there are several different methods for generating a constant pressure across the sample. They can range from using a pump (4) to elevating the fluid reservoir (15).

There are several limitations to the DC method, such as DC noise, drift, and concerns about electrode stability and polarization (3). Somasundaran and Kulkarni (2) claim to have made measurements for signals as small as 0.1 millivolt using the DC
Figure A.1. Typical DC streaming potential response. This data was collected on a glass filter with 70-90 μm pore diameters using $10^{-3}$ M KCl.
Figure A.2. DC streaming potential data of Figure A.1 versus the differential pressure across the sample is plotted. The straight line through the data is the least squares fit of the data which gives a coupling coefficient of $-1.32 \ \mu V/Pa$. 
method. However, when working with high-impedance samples it is difficult to make measurements as small as 0.1 millivolt because of signal-to-noise concerns. When working with rocks it is not uncommon to have streaming potential signals smaller than 0.1 millivolt. This is in the range where signal-to-noise concerns in DC measurements start to become prevalent. Another potential drawback of DC streaming potential measurements is the quantity of liquid required for the experiment. This can be a hindrance when working with limited amounts of liquid or liquids that are hazardous.

An advantage to the DC streaming potential measurements is the simplicity of the experiment. If small signals are not being measured, equipment needs are minimal. The equipment can be as simple as a good-quality voltmeter and a ruler used to measure pressure head. Consequently, no special pressure driving device is required to create a differential pressure across the sample.

A.4 Sinusoidal (AC) Streaming Potentials

Sinusoidal streaming potential signals (Figure A3) can also be analyzed to determine zeta potentials, since the surface-chemistry aspects of AC streaming potentials are the same as in the DC case. The main difference between the two methods is how the pressure is applied across the sample. In the DC case the pressure is constant and in the AC case the pressure is time varying. The following analysis of the sinusoidal data is based on looking at streaming potentials in the frequency domain. Consequently, equation (A1) now becomes
Figure A.3. Typical AC streaming potential response. This data was collected on a glass filter with 70-90 μm pore diameters using 10^{-3} M KCl.
\[ I_{\text{conv}}(\omega) = \int v(r, \omega) \rho_e(r) dr \quad . \]  

Integrating equation (A5) we find the frequency-dependent convection current to be

\[ I_{\text{conv}}(\omega) = \frac{2\pi e \alpha \zeta \Delta \rho(\omega)}{\eta \kappa} \frac{J_1(ka)}{J_0(ka)} \quad , \]  

where \( J_0 \) is a Bessel function of the first kind with order zero. \( J_1 \) is a Bessel function of the first kind with order one, and

\[ k = \sqrt{\frac{-i\omega\rho}{\eta}} \quad . \]  

The conduction current moving through the bulk fluid is also frequency dependent, since it must balance the convection current,

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

Setting the convection current equal to the conduction current gives

\[ C(\omega) = \frac{\Delta V(\omega)}{\Delta \rho(\omega)} = \left[ \epsilon \frac{\sigma}{T} \right] \frac{-2 J_1(ka)}{ka J_0(ka)} \quad , \]  

where \( C(\omega) \) is the frequency-dependent coupling coefficient. Equation (9) is referred to as the AC Helmholtz-Smoluchowski equation. The frequency at which inertial terms start to dominate over viscous terms is often called the transition frequency, and is given by
\[ \omega_t \equiv \frac{a^3}{8} \frac{\eta}{\rho}. \]  

[A10]

A thorough treatment of AC streaming potentials is given by Reppert and Morgan (11), and Pride (16).

### A.5 Sinusoidal Signal-Processing Techniques

There are several methods for processing and collecting the sinusoidal streaming potentials. We first present the processing techniques, followed by the collection methodologies. The first method of processing involves measuring the RMS signal for both the streaming potential and the differential pressure (1, 4, 5, 17). The ratio of the RMS streaming potential signal to the RMS pressure signal determines the streaming potential coupling coefficient. This method has the advantage of being computationally fast and not needing extensive data-acquisition equipment, but it has the disadvantage of having signal-to-noise problems. This method works well only when the measured signal is greater than any background noise. The main disadvantage of the RMS method is that any DC offset, such as from the electrodes, is included into the measurement. When using the RMS processing method, the phase of the pressure and voltage must be monitored to determine whether the coupling coefficient is negative or positive. If the signals are in phase the coupling coefficient is positive, and if they are out of phase the coupling coefficient is negative.
The second method of processing involves calculating the cross-correlation of both the streaming potential signal and the differential pressure signal and calculating the ratio of the cross-correlated signals. Cross-correlation can be accomplished by using either a reference signal or a noise-free differential pressure signal as the reference signal. This method has the advantage of having very good signal-to-noise characteristics, and of removing any DC offset from the measurement. If the measuring signals are in the microvolt range however, background noise can vary from frequency to frequency. This background noise can exceed or be a significant part of the measured signal. Because of the nature of cross-correlation measurements, there is no direct way of monitoring the noise at the measured frequencies.

The third method of processing the data uses spectral analysis. It involves calculating the amplitude spectrum of both the streaming potential and differential pressure signals. The cross-coupling response is obtained by taking the ratio of the streaming potential response to the differential pressure response (Figure A4). This method has the advantage of allowing the background noise to be determined at the measured frequency. After determining the background noise at the frequency of interest, a correction can be made or a different frequency can be chosen if necessary. Consequently, streaming potential measurements can be made to the microvolt or sub-microvolt range, depending on the quality of the electronics. Spectral analysis also allows the real and imaginary components of the coupling coefficient to be determined (10, 11). Another advantage is that DC offset can be completely removed from the data.
Figure A.4  a) The amplitude spectrum of the streaming potential and differential pressure across a porous glass filter with 70-90 μm pore diameters filled with $10^{-3}$ M KCl. The spectrums show a sinusoidal driving frequency of 26 Hertz. b) The coupling coefficient is found by dividing the SP amplitude spectrum by the pressure amplitude spectrum and reading the coupling coefficient at the driving frequency. At the driving frequency of 26 Hz the coupling coefficient is -1.3 μV/Pa. At frequencies other than the driving frequency, there is no signal, consequently the reading at frequencies other than the driving frequency are noise.
This method is computationally intensive compared to the other methods; this is its disadvantage.

The last method of data processing really requires no signal processing. In fact the time-varying streaming potential signal is plotted versus the time-varying differential pressure signal, and then the slope is calculated (Figure A.5). When calculating the slope using a least squares method, the large number of data points gives an accurate result. This method has the advantage of being simple and fast but has the disadvantage of requiring a good signal-to-noise ratio. This method must be used at a frequency lower than where inertial effects become evident in the fluid. Inertial effects become evident in the signals when a phase shift starts to occur between the streaming potential and pressure signals.

A.6 Sinusoidal Collection Techniques

There are three basic ways of collecting sinusoidal streaming potential data. One method of collecting the data is to keep the frequency stationary and vary the amplitude of the differential pressure across the sample. The amplitude of the driving pressure is then plotted versus the amplitude of the streaming potential response. This gives a plot of streaming potential versus pressure (Figure A.6), the slope of which is the coupling coefficient. It should be noted that all experiments described in this section were conducted on the same 70-90 µm sample using 10⁻³ M KCl. The result in Figure A.6 is identical to that obtained in DC experiments. (Figure A.2), also demonstrated by others (4, 5). Consequently this method of data acquisition is well suited for determining zeta potentials. This method has the advantage of giving a statistically accurate result whose
Figure A.5  The raw streaming potential data versus the raw differential pressure data is plotted for the same sample and chemistry as used in Figure A.2. The straight line shows the least squares fit of the data. The slope of the straight line gives a coupling coefficient of \(-1.29 \, \mu V/Pa\).
Figure A.6  This data was collected at a single frequency while varying the pressure on the same sample and chemistry as in Figure A.2. The straight line through the data is the least squares fit to the data whose slope gives a coupling coefficient of $-1.31 \, \mu V/\text{Pa}$. 
accuracy increases with additional measurements. The only disadvantage is that the measurements must be made well below the transition frequency if the DC limit of the coupling coefficient is desired. This method can be used with all AC data processing techniques.

Another collection method is to collect both streaming potential data and differential pressure data versus frequency (1, 5, 10, 11, 17). The measured voltage is divided by its corresponding pressure at each frequency to obtain the coupling coefficient at that frequency. The coupling coefficient can then be extrapolated to the DC limit in order to obtain the DC response (5, 10, 11). The theory for frequency-dependent streaming potentials (1, 11, 16) shows that the frequency-dependent streaming potential coupling coefficient remains constant at its DC limit until the critical frequency is approached, where the coupling coefficient then starts to decrease with increasing frequency. Figure A.7 shows an example of frequency-dependent cross-coupling data extrapolated back to the DC limit in order to obtain the DC coupling coefficient. In practice if the measurement is at an order of magnitude less than the critical frequency, it is not necessary to extrapolate to the DC limit. One can simply use the single frequency measurement and achieve the same result. It has also been demonstrated that capillary or pore radii can be obtained from frequency-dependent streaming potential data (10, 11). Therefore frequency-dependent streaming potential data can be used to determine zeta potentials as well as pore radii. As with the previous method, the greater the number of data points collected, the more accurate the results. This applies to multiple-frequency or
Figure A.7  Using the same sample and chemistry as in Figure A.2, the coupling coefficient versus frequency is shown using the AC method with the coupling coefficient theory also plotted. The DC limit gives a coupling coefficient of -1.31 μV/Pa.
single-frequency measurements. The RMS, cross correlation, and spectral analysis techniques all work with this collection method.

When collecting streaming potential data using a sinusoidal driving source, some precautions that should be taken to ensure high-quality data. One precaution is to electrically shield the sample and data-acquisition equipment from any EMF given off by the pressure driving device. This also has the advantage of minimizing 60 hertz noise which gives better signal-to-noise ratios for processing methods. Another precaution is to hold the sample securely to prevent any vibration from moving the sample or electrodes. If these precautions are taken, streaming potential measurements can routinely be made in the microvolt range if using the cross-correlation or spectral-analysis techniques. It should be pointed out that stacking of the data is required to achieve measurements in the microvolt range. The cross-correlation and spectral-analysis techniques also have the advantage of removing electrode effects from the measurements. The authors have made measurements and achieved equivalent results using stainless steel and silver silver-chloride electrodes.

A.7 Transient Streaming Potentials

Lastly, data can be collected using the transient method (8, 18), as shown in Figure A.8. Chandler (18) first used this method to monitor the Biot slow wave in porous media by monitoring the streaming potential response, but he did not determine coupling coefficients. Chandler developed the equation (A11), which relates the transient pressure
Figure A.8  Typical transient streaming potential response. This data was collected on a glass filter with 70-90 µm pore diameters using $10^{-3}$ M KCl.
pulse to the transient streaming potential between the center of a porous cylinder and the end of the cylinder:

$$V_s(t) = \frac{1}{2} V_o(t) \exp(-t/T_1)$$  \hspace{1cm} (A11)

Where $T_1$ is the characteristic time and

$$V_o(t) = \frac{\varepsilon \zeta}{\eta \sigma} p_o(t)$$  \hspace{1cm} (A12)

The development of equation (A11) is based on inertial terms not being present in the solution. This occurs when the frequencies constituting the transient are an order of magnitude less than the transition frequency. The limitation of equation (A11) is evident when plotting raw transient streaming potential data versus raw transient pressure data Figure A.9. The data in Figure A.9 show a curved part, which is related to the inertial part of Figure A.10 which coupling coefficient spectral response data collected on the same sample. The straight-line part of Figure A.9 is related to the non-inertial region in Figure A.10. Calculating the slope of the non-inertial region of Figure A.6 gives a coupling coefficient of 2.0 $\mu$V/Pa. The frequency-domain analysis gives a coupling coefficient of 1.26 $\mu$V/Pa. The frequency-domain analysis is in agreement with the coupling coefficient analysis done using the other methods on the Porous Filter B sample.

When calculating the slope of curve of the streaming potential versus pressure it appears that the data do not account for the phase difference that can occur between the
Figure A.9 Using the same sample and chemistry as in Figure A.8, the raw data of the transient method is plotted with a least squares fit to the straight line portion of the curve. The best fit line through the data gives a coupling coefficient of $-1.99 \mu V/ Pa$. 
Using the same sample and chemistry as in Figure A.8, the coupling coefficient versus frequency is shown using the transient method. The best fit line through the non-inertial region of the data gives a coupling coefficient of $-1.26 \mu V/\text{Pa}$. 

Figure A.10
streaming potential signal and the pressure signal. The phase difference for the Porous Filter B starts to occur at frequencies much lower than the transition frequency, as can be seen in the Porous Filter B theoretical phase (Figure A.11). When comparing the theoretical plot in Figures A.7 and A.11, it can be seen that the phase shows the inertial effects much earlier than the magnitude data of Figure A.7. If the transient has no inertial effects, a plot of streaming potential versus pressure similar to the plot in Figure (A.12) can be achieved. Figure A.12 shows the plot of streaming potential versus pressure for a transient on Berea Sandstone. The same coupling coefficient is obtained when using the frequency-domain analysis on the same Berea Sandstone sample. It should be noted that the long-time part of the transient (low-frequency part) usually has a very poor signal-to-noise ratio and should be avoided in the processing. Possible uses of the transient method when the streaming potential data are plotted versus pressure data is to obtain coupling coefficients and zeta potentials where DC and AC techniques are not feasible.

The best processing method to obtain information on coupling coefficients when using the transient collection method is to take the Fourier transform of the data and divide the streaming potential signal by the pressure signal (Figure A.10). This analysis is based on the frequency-domain analysis presented in the sinusoidal section. When using the frequency-domain analysis, errors associated with inertial effects can be avoided. To accomplish this, the coupling coefficient is read from the zero-slope part of the frequency-domain coupling coefficient. As mentioned in the last paragraph, the signal-to-noise in the low-frequency part of the data can be poor. Therefore, when
Figure A.11  Theoretical plot of phase versus frequency for the Porous B Filter. Comparing this figure to Figure A.8, it can be seen that inertial effects are present much sooner in the phase data than the magnitude data. The transition frequency $f_t$ of 710 Hz is shown in the figure. The transition frequency is the frequency at which inertial effects start to dominate over viscous effects.
Figure A.12  Transient streaming potential data plotted versus transient differential data for Berea Sandstone. The chemistry was initially di-ionized water that was allowed to come to equilibrium with the rock over time. The slope of the least squares fit line gives a coupling coefficient of -4.3 mV/Bar, which is in agreement with the values obtained using the sinusoidal spectral analysis method.
fitting the frequency-dependent coupling coefficient theory, equation [A9], to the transient data, low frequencies should be avoided. It is also useful to look at the streaming potential and pressure spectra individually to see at what frequency the signal-to-noise ratio starts to skew the coupling coefficient data. Applications for the spectral analysis technique of analyzing transient data are to determine zeta potentials and the average pore size of the sample.

The data-analysis methods available for looking at transient data is limited to spectral analysis and the plotting of the streaming potential data versus the pressure data and then calculating the slope. These two techniques are applied in the same way as described in the sinusoidal signal-processing techniques.

When working with the transient method of collecting data, the limitations due to inertial effects and poor signal-to-noise ratios can be minimized. To minimize the problems associated with the to poor signal-to-noise ratios, sufficiently large streaming potential signals must be generated in order to get a better signal-to-noise ratio at the low frequencies. This requires an initial high-pressure pulse. At the end of the transient (low-frequency component) the signal-to-noise ratio will be poor. However, the initial high-pressure pulse may have increased the signal-to-noise ratio enough to get usable data for use in data processing. If the transient has high-frequency components, inertial effects may also be included in the data. Also, if the sample permeability is high, most of the data with good signal-to-noise ratios may include inertial effects. Consequently, when calculating the slope of curve of streaming potentials versus pressure to determine the
coupling coefficient, it is best to have the sample permeability sufficiently low that inertial effects are absent or at least minimized. Data on streaming potential versus pressure have been successfully collected on Berea Sandstone, which can have a porosity as high as 20% and permeability as high as 500 mD. When analyzing transient data by the spectral-analysis technique, the limitation is also the signal-to-noise ratio at low frequencies. If it is desired to see both the critical frequency and the DC limit of the coupling coefficient, two separate transients (with different frequency components) may have to be used to get accurate data in the frequency range of interest. It should be noted that when using the spectral-analysis technique, spurious results may be obtained if the DC value at the beginning of the transient is not the value as that at the end of the transient. In other words, step-function transients should be avoided.

When collecting data on transient streaming potential there are two precautions to be take to ensure quality data. First, the sample and data-acquisition equipment needs to be electrically shielded from any EMF in the laboratory. This increases the signal-to-noise ratio in the long-time part of the transient. Second, the sample should be securely held to prevent any vibration of the sample or electrodes. If these precautions are taken when using the spectral-analysis technique, streaming potential measurements can be made in the microvolt range. Stacking of the data is required to achieve microvolt-range measurements. The authors have made measurements using the transient method and achieved equivalent results using stainless steel and silver silver-chloride electrodes.
The transient method has the advantage of not requiring a sinusoidal source to drive the pressure. However, significantly more stacking of the data is usually required because the poor signal to noise ratio of the transient method.

A.8 Summary

Data-processing and collection techniques have been presented for DC, sinusoidal, and transient streaming potential data. The data shown in the figures were collected within one hour using the same sample with identical chemistry for each technique, except the transient raw data technique (Figure A.12). The data-processing results agree within 1.8% for all processing methods when using the sinusoidal collection technique. The coupling coefficient measured using different collection technique agree within 3.1%, with the transient method having the worst standard deviation. The advantages and disadvantages of each technique have been discussed. Each collection technique and processing method may lend its use to particular experiments. If the measurements have good signal-to-noise ratios, any of the techniques will give adequate results. If the measurements are on samples with poor signal-to-noise ratios, the sinusoidal collection technique using spectral analysis or cross-correlation to process the data will give superior results. At the present time the transient technique has limited applications because of signal-to-noise issues.
A.9 References


13. Hunter, R. J., “Zeta Potential in Colloid Science: Principles and Applications.”,


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Figure A.1. Typical DC streaming potential response. This data was collected on a glass filter with 70-90 μm pore diameters using 10^{-3} M KCl.

Figure A.2. DC streaming potential data of Figure 1 versus the differential pressure across the sample is plotted. The straight line through the data is the least squares fit of the data which gives a coupling coefficient of -1.32 μV/Pa.

Figure A.3. Typical AC streaming potential response. This data was collected on a glass filter with 70-90 μm pore diameters using 10^{-3} M KCl.

Figure A.4 a) The amplitude spectrum of the streaming potential and differential pressure across a porous glass filter with 70-90 μm pore diameters filled with 10^{-3} M KCl. The spectrums show a sinusoidal driving frequency of 26 Hertz. b) The coupling coefficient is found by dividing the SP amplitude spectrum by the pressure amplitude spectrum and reading the coupling coefficient at the driving frequency. At the driving frequency of 26 Hz the coupling coefficient is -1.3 μV/Pa. At frequencies other than the driving frequency, there is no signal, consequently the reading at frequencies other than the driving frequency are noise.

Figure A.5 The raw streaming potential data versus the raw differential pressure data is plotted for the same sample and chemistry as used in Figure 2. The straight line shows the least squares fit of the data. The slope of the straight line gives a coupling coefficient of -1.29 μV/Pa.

Figure A.6 This data was collected at a single frequency while varying the pressure on the same sample and chemistry as in Figure 2. The straight line through the data is the least squares fit to the data whose slope gives a coupling coefficient of -1.31 μV/Pa.

Figure A.7 Using the same sample and chemistry as in Figure 2, the coupling coefficient versus frequency is shown using the AC method with the coupling coefficient theory also plotted. The DC limit gives a coupling coefficient of -1.31 μV/Pa.

Figure A.8 Typical transient streaming potential response. This data was collected on a glass filter with 70-90 μm pore diameters using 10^{-3} M KCl.

Figure A.9 Using the same sample and chemistry as in Figure A.8, the raw data of the transient method is plotted with a least squares fit to the straight line portion of the curve. The best fit line through the data gives a coupling coefficient of -1.99 μV/Pa.

Figure A.10 Using the same sample and chemistry as in Figure A.8, the coupling coefficient versus frequency is shown using the transient method. The best fit line through the non inertial region of the data gives a coupling coefficient of -1.26 μV/Pa.
Figure A.11 Theoretical plot of phase versus frequency for the Porous B Filter. Comparing this figure to Figure (8), it can be seen that inertial effects are present much sooner in the phase data than the magnitude data. The transition frequency $f_t$ of 710Hz is shown in the figure. The transition frequency is the frequency at which inertial effects start to dominate over viscous effects.

Figure A.12 Transient streaming potential data plotted versus transient differential data for Berea Sandstone. The chemistry was initially de-ionized water that was allowed to come to equilibrium with the rock over time. The slope of the least squares fit line gives a coupling coefficient of $-4.3 \text{ mV/Bar}$, which is in agreement with the values obtained using the sinusoidal spectral analysis method.