A Chemical Reaction-based Boundary Condition for Flow Electrification

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ABSTRACT
A physical model is developed for the charge transfer boundary condition in semi-insulating liquids. The boundary condition is based upon interfacial chemical reactions and extends established relations for the interface by including the effects of interfacial surface charge and charge desorption at the interface. A steady state model for flow electrification in a rotating cylindrical electrode apparatus incorporated this boundary condition and described polarity changes in the open-circuit voltage and short-circuit current as a function of the fluid velocity, the volume charge density dependence on the terminal constraints, and the charge density dependence on applied dc voltages. Previously used boundary conditions are shown to be special cases of the chemical reaction rate boundary condition. A general methodology is developed for combining the volume charge density and voltage/current terminal measurements to estimate the parameters describing the interfacial charge transfer kinetics. Volume charge densities \( \rho^w \) on the liquid side of the interfaces of 1 to 20 mC/m\(^3\) were estimated from the open-circuited electrode measurements, with the stainless steel \( \rho^w \) typically larger than that of copper but smaller than that of transformer pressboard. Activation energies for an Arrhenius temperature dependence of \(-0.16\) eV for pressboard, 0.25 eV for stainless steel and 0.28 eV for copper were obtained. Interfacial adsorption reaction velocities, estimated to be \(10^{-5}\) m/s, were not large enough to make the terminal current transport limited which contradicts the often used assumption that the reaction velocities can be considered 'infinite'. Estimated surface reaction rates at a 70°C stainless steel/oil interface of \(-20\) \(\mu\)m/s for adsorption and \(-0.5\) s\(^{-1}\) for desorption were obtained. The additive BTA reduced the \( \rho^w \) for pressboard and stainless steel at concentrations > 8 ppm in transformer oil.

1. INTRODUCTION

Although the interfacial charge transfer between the solid and liquid phase is a fundamental process in flow electrification, it is not well understood. Indeed, it is the preferential adsorption of one of the charged species that leads to the generation of the electrical double layer and it is the diffuse charge in the double layer that is transported by the fluid to accumulate or leak away at a downstream location. Unfortunately, since the ions responsible for the conduction in the liquid are usually unknown and present in trace quantities, the boundary conditions are usually postulated [1–8]. A physicochemical derivation of the boundary condition has been developed recently but important physical mechanisms, such as charge desorption at the interface, were omitted [9]. In this paper a physicochemical approach is used to develop a charge transfer boundary condition that includes the effects of charge desorption in the presence of a surface charge density. This extended boundary condition is necessary to explain some of the results in [10, 11] that could not be explained by the standard flow electrification boundary conditions of specifying the wall charge density, the zeta potential, or the spatial derivative of the charge density at the wall.

As a specific application, the chemical reaction based boundary condition is also incorporated into a model for flow electrification between two rotating concentric cylinders. The rotating cylinders create fluid flow which results in a net charge density in the bulk region of the liquid between the electrodes and a net voltage across or current through the electrode terminals. While the terminal current or voltage from the electrode may be related to the parameters describing the interfacial reaction [12], direct measurements of the volume charge density are also possible for the semi-insulating materials of interest in electric power apparatus [7, 8, 13]. The electrification model provides self-consistent relations between the bulk charge density, the terminal variables, and parameters which describe the interfacial processes. Using the extended boundary condition developed here, the model is able to explain polarity changes in terminal open-circuit voltage and short-circuit current as...
a function of fluid flow rate, slight variations in the volume charge density as the electrical terminals are open or short-circuited, and changes in the volume charge density with applied dc voltages.

This paper begins with a review of the fundamental processes involved in flow electrification and then provides a general discussion of the pertinent physicochemical boundary conditions. Subsequent sections then provide simplified example applications of the boundary condition. The boundary condition is first applied to a single, isolated interface and the interfacial reaction rates are related to the commonly referenced zeta potential. Justification for simplifying the interfacial reactions of two individual ionic species in terms of the net current density and charge density is also presented. The boundary condition is then applied to the case of stationary concentric cylindrical electrodes and then the case of a rotating inner electrode so that the flow induced volume charge density and terminal quantities are related to the interfacial parameters. The model is then compared to several sets of experimental measurements to test the validity of the boundary conditions and estimate the charge transfer reaction rates at the liquid/solid interface and the interfacial parameter dependence on the concentration of the antistatic additive BTA (1,2,3-benzotriazole).

2. BASIC FORMULATION

The process of flow electrification involves the generation, transport, accumulation, and leakage of electrical charge. This section presents a general framework for modeling the electrification processes.

2.1. FLUID BULK REPRESENTATION

Even in a highly purified state, the fluid will contain impurities that can undergo chemical reactions and affect the charge generated by flow electrification. Since these impurities are usually present in trace amounts, their composition tends to be unknown. For the purposes of this model, a single ionizable impurity is assumed. A model for the chemical reaction involving this impurity is based on the assumption that there are three reacting species which obey the ion reaction [14]

\[ \gamma C \overset{k_{d}}{\rightleftharpoons} A^{+z} + B^{-z} \] (1)

where \( C \) dissociates into a positive ion \( A \) and a negative ion \( B \), \( k_{d} \) is the dissociation rate constant, \( k_{r} \) the recombination rate constant, and \( z \) is the valence charge of the ions. The factor \( \gamma \) represents the molecularity of the reaction [15]. For example, when \( \gamma = 1 \), the reaction is unimolecular when molecule \( C \) decomposes into the products \( A \) and \( B \), but bimolecular when \( A \) and \( B \) combine to form \( C \). When \( \gamma = 2 \), both the forward and reverse reactions are bimolecular and 2 molecules of \( C \) are involved in the reaction. The molecularity is an empirical result that depends upon the species involved in the chemical reaction; the molecularity equals half the slope of the logarithm of the conductivity plotted vs. the logarithm of the concentration of \( C \) [16].

As a result of the chemical reactions, the concentrations of the species will change with time. The equations that describe these chemical kinetics for uniform concentrations are

\[ \frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{1}{\gamma} \frac{d[C]}{dt} \]

\[ = k_{d}[C]^{\gamma} - k_{r}[A^{+z}][B^{-z}] \] (2)

where the \([X]\) symbols denote the molar concentration or number density of species \( X \). The first term on the right side of Equation (2) gives the rate of generation of ions \( (A^{+z} \text{ and } B^{-z}) \) from the dissociating neutral molecule \( C \), while the second term gives the rate of recombination of the ions to form the neutral molecule. While this description of chemical kinetics is valid for a fully mixed system, most systems have spatial variations. A general formulation for the kinetics can be derived by balancing the time rate of change of the concentration of each species in a differential volume to the flux through the surface enclosing the volume and any chemical reactions inside the volume. This conservation equation can be written as [17]

\[ \frac{\partial n_{i}}{\partial t} + \nabla \cdot \Gamma_{i} = G_{i} - R_{i} \] (3)

where the subscript \( i \) denotes the \( i \)th species, \( n_{i} \) is the number density, \( \Gamma_{i} \) is the flux, and \( G_{i} \) and \( R_{i} \) represent the generation and recombination due to the chemical reactions. This is equivalent to Equation (2) if the convective derivative is taken.

The flux term gives the transport of each species through the fluid. It is generally stipulated by a constitutive law that accounts for diffusion, convection, and drift if the species is charged. For the \( i \)th species, the flux can be expressed as [18]

\[ \Gamma_{i} = -D_{i}\nabla n_{i} + n_{i}\bar{v} + \frac{z_{i}}{|z_{i}|}b_{i}n_{i}\bar{E} \] (4)

where \( D_{i} \) is the diffusivity, \( \bar{v} \) the fluid velocity, \( z_{i} \) the valence number, \( b_{i} \) the ion mobility if the species is charged (\( z_{i} \neq 0 \)) and \( \bar{E} \) is the electric field. A neutral species does not have a drift component to the flux and can be considered as having zero mobility. The diffusivity and mobility are related through the Einstein relation

\[ \frac{D_{i}}{b_{i}} = k_{B}T \]

(5)

where \( k_{B} = 1.38 \times 10^{-23} \text{ J/K} \) is Boltzmann’s constant, \( T \) the absolute temperature and \( q = 1.6 \times 10^{-19} \text{ C} \) is the elementary electronic charge. The diffusion flux is based on Fick’s law and the assumption that the species are present in trace quantities so that each species diffuses independently [19]. Assuming that the system is electroquasistatic, the electric field can be determined from the electric scalar potential \( \Phi \) and the net free charge through Gauss’ law as

\[ \bar{E} = -\nabla \Phi \]

(6)

where \( \varepsilon \) is the dielectric permittivity and \( \rho \) is the net free volume charge density. It is also assumed that the fluid is an incompressible liquid with the flow imposed by an external mechanical system. This implies that any electrical forces on the charged fluid are negligibly small so that the fluid mechanics are decoupled from the electrical laws.

The generation and recombination terms in Equation 3 can be expressed in a more explicit form when the chemical reactions in the bulk of the liquid are specified. As an example, consider the three species reaction given by Equation (1). In the absence of spatial gradients, when the fluid is fully mixed, Equations (2) and (3) have the same form. If the
species are identified by
\[ n_{A^+} = [A^+] \]
\[ n_{B^-} = [B^-] \]
\[ n_C = [C] \]
the generation and recombination terms can be expressed as
\[ G_{A^+} = G_{B^-} = \frac{1}{\gamma} R_C = k_d n_C \]  
\[ R_{A^+} = R_{B^-} = \frac{1}{\gamma} G_C = k_r n_{A^+} n_{B^-} \]  
The terms \( R_C \) and \( G_C \) are divided by the factor \( \gamma \) because it takes \( \gamma \) moles of the neutral molecule \( C \) to produce one mole of the ions \( A^{\pm} \) and \( B^{\pm} \).

2.2. BOUNDARY CONDITIONS

In addition to the equations describing the dynamics of the charged species in the bulk of the fluid, the boundary conditions imposed by the interface between the solid and liquid phases also must be considered. The interface between the liquid and the solid phases is taken to be an infinitely thin region (in the continuum sense) which imposes boundary conditions on the bulk relations for the chemical species and the electric field.

In order for a net current to pass between the fluid phase, the solid phase and an external circuit, a chemical (redox) reaction must occur at the interface or a charged species must accumulate at the interface. Both of these processes can be described as heterogeneous reactions because they occur between two different phases. The basic steps for heterogeneous reactions are: the transport of reactants to the surface, the adsorption of reactants onto the surface, the reaction on the surface, the desorption of reactants (products) from the surface, and the transport of reactants (products) away from the surface [20]. The transport mechanism to and from the surface is usually taken to be diffusion, but fluid convection and the migration of charged species also serve as transport mechanisms as given by Equation (4). The surface reaction, adsorption and desorption processes lead to the boundary conditions on the flux of species to the interface.

Consider the adsorption of reactants to the interface. The species can be adsorbed from the liquid side of the interface into vacancies on the interface according to the ionic equations
\[ A^{\pm} + V_+ \xrightarrow{k'_f} SA^{\pm} \]  
\[ B^{\pm} + V_- \xrightarrow{k'_f} SB^{\pm} \]  
\[ C + V \xrightarrow{k'_f} SC \]  
where \( V_+ \), \( V_- \), and \( V \) are the vacant sites available to each respective species, \( SA^{\pm} \), \( SB^{\pm} \), and \( SC \) are the adsorbed species at the interface and \( k'_f \) denote reaction rates for the forward (\( j = f \)) and reverse (\( j = r \)) reactions for the \( i \)th species (\( +, -, C \)). The vacant sites represent the microscopic locations where the chemical reactions occur.

Related examples are the diffusion of calcium through muscle with binding sites in the tissue [18], the surface states associated with the triboelectric contact charging of toner particles [21] and the surface states that can be present at semiconductor interfaces [22].

Once at the interface, the species can be involved in a redox reaction, typically transferring electrons, but proton transfer may also occur [14]. Assuming, for simplicity, that only electron transfer occurs and that the adsorbed neutral \( SC \) is not involved in these redox reactions, the ionic equations are
\[ SA^{\pm} + ze^{-} \xrightarrow{k_{SA}} SA \]  
\[ SB^{\pm} \xrightarrow{k_{SB}} SB + ze^{-} \]  
where \( SA \) and \( SB \) denote adsorbed neutral species at the interface. These new constituents can be desorbed from the interface to the liquid side of the interface according to
\[ SA \xrightarrow{k_{SA}} A + V_+ \]  
\[ SB \xrightarrow{k_{SB}} B + V_- \]  
Thus, in addition to the three original reacting species in the bulk \( (A^{\pm}, B^{\pm}, \text{and } C) \) two more neutral species \( (A \text{ and } B) \) are also present.

Associated with each of the chemical reactions is a kinetic equation. For example, the kinetic equations for the surface states involved in the adsorption processes of the ionic species can be expressed as
\[ \frac{d[SA]}{dt} = -\frac{d[V_+]}{dt} = -\frac{d[A^{\pm}]}{dt}k_b^{\pm}[SA^{\pm}] \]  
\[ \frac{d[SB]}{dt} = -\frac{d[V_-]}{dt} = -\frac{d[B^{\mp}]}{dt}k_b^{\mp}[SB^{\mp}] \]  
where the concentrations of species at the liquid side of the interface have the superscript \( b \) to indicate the concentration at the liquid boundary. In order to couple these kinetic equations to the conservation equations for the species in the bulk regions, conservation equations can also be written for the species at the surface. Similar to Equation (3), the conservation equation for the surface number density \( \sigma \) of the \( i \)th species can be written as
\[ \frac{\partial \sigma_i}{\partial t} + \vec{n}_s \cdot \vec{\nabla} \sigma_i = G'_{i} - R'_{i} \]  
where the symbol \( \| \vec{\nabla} \| \) denotes the difference in fluxes on either side of the interface, \( \vec{n}_s \) is the unit vector normal to the interface and pointing from the liquid into the solid, and \( G'_{i} \) and \( R'_{i} \) are the surface generation and recombination rates due to the redox reactions. Letting the surface density \( \sigma_X \) denote the surface concentration \( [SX] \), the conservation equations for the surface densities become
\[ \frac{\partial \sigma_{A^+}}{\partial t} - \vec{n}_s \cdot \vec{\nabla} \sigma_{A^+} = -(k_{SA}^{f} \sigma_{A^+} - k_{SA}^{r} \sigma_A) \]  
\[ \frac{\partial \sigma_{B^-}}{\partial t} - \vec{n}_s \cdot \vec{\nabla} \sigma_{B^-} = -(k_{SB}^{f} \sigma_{B^-} - k_{SB}^{r} \sigma_B) \]  

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where the fluxes $\hat{n}_s \cdot \Gamma_{A+}^{b}$ give the flux of the species from the liquid phase into the solid phase as

$$\hat{n}_s \cdot \Gamma_{A+}^{b} = k^i_+ n^{b+}_{A+} \sigma V_+ - k^-_+ \sigma A+$$  \hspace{1cm} (22)

$$\hat{n}_s \cdot \Gamma_{B-}^{b} = k^i_- n^{b-}_{B-} \sigma V_- - k^-_- \sigma B-$$  \hspace{1cm} (23)

These fluxes provide the necessary interfacial boundary conditions for the equations describing the species densities in the bulk region.

For this model, the reaction rates $k^i_+$ are assumed to be independent of the applied voltage. Although small electric fields are considered in most of this analysis, and large fields usually are necessary for voltage dependent reaction rates, as in Onsager field enhanced dissociation [23], it has been shown that externally applied electrical potentials influence the activation energy of some aqueous electrolytic reactions, as in the Tafel equation [24]. Since the potential difference that enters into the Tafel equation is essentially that across the thin interfacial 'Stern' layer, which is relatively large compared to the diffuse portion of the double layer in aqueous solutions but small in the nonaqueous semi-insulating solutions of interest here, it appears reasonable to assume that the dynamics will be dominated by the diffuse portion of the double layer and the interfacial reaction rates can be taken as independent of the applied potential.

It is worth noting that some of the conventional electrification boundary conditions are similar in form to Equations (22) and (23). For example, it has been postulated that the interfacial flux of each individual species is linearly related to the difference between the volume density of the species near the interface and the equilibrium density. For the two charged species of Equation (1), this can be written as

$$\hat{n}_s \cdot \Gamma_{A+} = k^i_+ (n^{b+}_{A+} - n^{w+}_{A+})$$  \hspace{1cm} (24)

$$\hat{n}_s \cdot \Gamma_{B-} = k^i_- (n^{b-}_{B-} - n^{w-}_{B-})$$  \hspace{1cm} (25)

where $\hat{n}_s$ is a unit vector normal to the interface and pointing into the solid and the parameters $k^i_+$ and $n^{w+}_{A+}$, $n^{w-}_{B-}$ are constants for the interface at a given temperature and the superscript $b$ denotes the carrier density on the liquid side of the interface [3, 5, 6]. With the charge transfer attributed to an oxidation-reduction process occurring at the interface, $k^i_+$ can be considered a reaction velocity and $n^{w+}_{A+}$ can be considered the equilibrium carrier density in the absence of any current flow. Another form of this boundary condition is expressed in terms of the net current density $\vec{J} = qz(\vec{\Gamma}_{A+} - \vec{\Gamma}_{B-})$ and the charge density $\rho = qz(n^{A+} - n^{B-})$ as

$$\hat{n}_s \cdot \vec{J} = k^i_o (p^b - p^w)$$  \hspace{1cm} (26)

where $k^i_o$ represents a surface reaction velocity and $p^w$ represents the equilibrium wall charge density in the absence of a current [4]. This expression follows from Equations (24) and (25) by setting $k^i_o = k^i_+ = k^i_-$. $p^b = qz(n^{b+}_{A+} - n^{w-}_{A+})$ and $p^w = qz(n^{w+}_{B-} - n^{w-}_{B-})$.

For the boundary condition on the electric field, with the interface able to support a net surface charge, the normal component of the electric field can be discontinuous across the interface. Applying Gauss' law to the interface

$$\hat{n} \cdot || \vec{D} || = q \sum \epsilon_i \sigma_{i\pm} = \sigma_{st}$$  \hspace{1cm} (27)

where $\hat{n}$ is a unit vector normal to the interface, $\vec{D}$ is the displacement field, $\sigma_{i\pm}$ is the surface number density of the $i$th species, $\sigma_{st}$ is the free surface charge density and $|| \vec{D} ||$ denotes the jump discontinuity in $\vec{D}$. When the surface charge is time varying, charge conservation requires

$$\hat{n} \cdot || \vec{J} || = \hat{n} \cdot q \sum \epsilon_i \vec{J}_i = - \frac{\partial \sigma_{st}}{\partial t}$$  \hspace{1cm} (28)

This condition is necessary if the solid is represented by a single conductivity but redundant when all of the conservation equations for all of the species (e.g., positive and negative ions or even holes and electrons) have been specified. The electric potential is also continuous across the interfaces.

Although this provides a self-consistent description for both the bulk and the interfacial dynamics, these results need to be more specific to be useful in electrification models. The large number of parameters for describing the interfacial charge transfer, when coupled with the model for the charge dynamics in the bulk of the liquid and solid, exceeds our experimental ability to determine the parameters uniquely. As a result, additional simplifying assumptions are made.

3. STATIONARY INTERFACE

Before fluid flow is introduced, it is useful to explore some of the implications of these chemical reaction based boundary conditions. In particular, for an isolated interface the zeta potential is related to the interfacial reaction rates and a useful form for the boundary condition on electrical current density at the interface is derived. Applying this boundary condition to a dielectric fluid placed between two concentric electrodes then illustrates the effect of the reaction rates and the applied voltage on the charge and field distributions.

![Figure 1. An isolated interface between solid and liquid dielectrics.](image)

The solid is a homogeneous, ohmic conductor with a single permittivity and conductivity. The liquid has both positive and negative charges that have been created by the dissociation of a single ionizable constituent. The bulk of the liquid is grounded by a perfectly conducting electrode at $z = \infty$. Shown is a preferential adsorption onto the solid/liquid interface so that the zeta potential is negative.

3.1. ISOLATED INTERFACE

Consider a single liquid/solid planar interface that is far from all electrodes, as shown in Figure 1. With the electrodes far from the interface, any preferential adsorption of one polarity of charge species onto the interface will be imaged by the mobile charge on the liquid side of the interface, assuming that the solid is an ohmic conductor represented by a single conductivity and permittivity. If there is a preferential adsorption, a potential difference will develop between the interface and the bulk region of the liquid. At equilibrium this interfacial potential is the
zeta potential \( \zeta \) and the corresponding distribution in mobile charge carriers is the electrical double layer. When a net current flows, the interface is no longer at equilibrium and the interfacial potential deviates from the zeta potential. The width of the interfacial space charge layer near the solid/liquid interface is of the order of the Debye length, and much thinner than any other system dimension. We thus only consider one dimensional variations with the \( x \) coordinate.

### 3.1.1. Equilibrium Case

In equilibrium the flux of each individual species is zero everywhere. This specification has the effect of decoupling the distributions of the charged species from the neutrals and Equation (4), with \( \dot{\psi} = 0 \), indicates that the neutral (\( b = 0 \)) species have a uniform distribution with generation balancing recombination. Using Equation (4) with the fluid velocity and the fluxes set to zero, Einstein’s relation (Equation (5)) and \( z_{A^+} = -z_{B^-} = z \) gives the carrier densities as

\[
n_{A^+}(x) = n_o \exp \left[ \frac{z_q \Phi(x)}{kT} \right]
\]

where boundary conditions at \( x = \infty \) of charge neutrality (\( n_{A^+} = n_{B^-} = n_o \)) and zero potential have been imposed. Substitution into Gauss’ law (Equation (6)) then gives the Poisson-Boltzmann equation for the potential as

\[
\kappa^2 \frac{d^2 \Phi}{dx^2} \left( \frac{z_q \Phi}{kT} \right) = \sinh \left( \frac{z_q \Phi}{kT} \right) = -\frac{\rho}{2qzn_o}
\]

where

\[
\kappa = \sqrt{\frac{\varepsilon kT}{2q^2z^2n_o}}
\]

is the Debye length. The corresponding electric field is

\[
E_x = -\frac{d\Phi}{dx} = \frac{2kT}{\kappa z} \sinh \left( \frac{qz \Phi}{2kT} \right)
\]

where in obtaining this result a square root was taken with the sign chosen so that the electric field is positive for positive potentials. By integrating from 0 to \( x \) and rearranging, the potential can be written explicitly as

\[
\Phi = \frac{2kT}{qz} \ln \left[ \frac{1 + \tanh \left( \frac{qz \Phi}{4kT} \right)}{1 - \tanh \left( \frac{qz \Phi}{4kT} \right)} \exp \left[ -\frac{x}{\kappa} \right] \right]
\]

where \( \zeta \) is the potential at \( x = 0 \). Note that for a weak double layer, \( \kappa \ll kT/qz \) and the potential is approximated by

\[
\Phi \approx \zeta e^{-x/\kappa}
\]

This shows that the potential decays exponentially with distance away from the interface when the zeta potential is small.

The interfacial parameters are also related to the zeta potential. Consider first the conventional boundary condition of Equation (24) and (25). In equilibrium, there is no net flux of ionic species to the interface so the carrier densities have their equilibrium value of \( n_{A^+, B^-} \). Using Equation (29), these carrier densities are related to the zeta potential by

\[
n_{A^+}(x = 0) = n_{A^+}^\nu = n_o e^{-qz \zeta /kT}
\]

\[
n_{B^-}(x = 0) = n_{B^-}^\nu = n_o e^{qz \zeta /kT}
\]

so that \( n_{A^+}^\nu \) and \( n_{B^-}^\nu \) are not independent. If the temperature, ion mobilities, and the conductivity \( \sigma_2 \equiv qzn_o (b_{A^+} + b_{B^-}) \) are known, then the ‘wall’ carrier densities can be calculated from the zeta potential. This implies that the zeta potential is a fundamental parameter of the interface, independent of the reaction velocities \( k_{\pm} \). Although this is consistent with the hypothesis that the reaction velocities are nonequilibrium parameters and only involved when current flows across the interface, it is inconsistent with the physical understanding of the zeta potential reflecting the preferential adsorption or an imbalance in interfacial reaction rates of the charged species.

Next consider the chemical reaction based boundary condition of Equations (22) and (23). To obtain the relation between the zeta potential and the reaction rates, first notice that the free surface charge density on the solid/liquid interface is

\[
\sigma_{su} = qz (\sigma_{A^+} - \sigma_{B^-}) = eE_x|_{x=0}
\]

as long as the electric field inside the solid is negligible. For example, the electric field is zero for a perfectly conducting material or an ionic material with zero current density. With the equilibrium assumption requiring the flux of each species to be zero at the interface, the species density on the liquid side of the interface is related to the surface density according to Equations (22) and (23), as

\[
k_{+}^\nu \sigma_{A^+} = k_{+}^\nu n_{A^+}^\nu \sigma_{V^+}
\]

\[
k_{-}^\nu \sigma_{B^-} = k_{-}^\nu n_{B^-}^\nu \sigma_{V^-}
\]

In principle, the surface densities of the vacant sites for the charged species (\( \sigma_{V^\pm} \)) are related to the charge transfer and desorption reactions. Since little is known about these reactions, the approach used in modeling the diffusion of calcium ions through muscle [18] is applied and it is assumed that the surface density can be written as

\[
\sigma_{V^+} = \sigma_{A^+}^s - \sigma_{A^+}
\]

\[
\sigma_{V^-} = \sigma_{B^-}^s - \sigma_{B^-}
\]

where \( \sigma_{A^+}^s \) is the surface saturation density for \( A^+ \) and \( \sigma_{B^-}^s \) is the surface saturation density for \( B^- \). Physically, this implies that the total number of states (filled and unfilled) for each species remains constant. The bulk-phase species density near the interface is then related to the interfacial surface density by

\[
K_+ n_{A^+}^b = \frac{\sigma_{A^+}^s - \sigma_{A^+}}{\sigma_{A^+} - \sigma_{A^+}^s}
\]

\[
K_- n_{B^-}^b = \frac{\sigma_{B^-}^s - \sigma_{B^-}}{\sigma_{B^-} - \sigma_{B^-}^s}
\]

with \( K_+ \equiv k_{+}^\nu /k_{+}^\nu \) and \( K_- \equiv k_{-}^\nu /k_{-}^\nu \) defined as equilibrium rate constants for the positive and negative charge carriers. These expressions are in the form of the classical Langmuir isotherm for the equilibrium adsorption of species on an interface [25]. Solving for the carrier surface densities in Equations (42) and (43) and then combining with Equations (29), (32) and (37) then yields

\[
\sinh \left( \frac{qz \zeta}{2kT} \right) = \frac{1}{4\lambda} \times \left( \frac{K_+ \exp \left[ -\frac{qz \zeta}{kT} \right] \sigma_{A^+}^s - K_- \exp \left[ \frac{qz \zeta}{kT} \right] \sigma_{B^-}^s}{1 + K_+ n_o \exp \left[ -\frac{qz \zeta}{kT} \right] - 1 + K_- n_o \exp \left[ \frac{qz \zeta}{kT} \right]} \right)
\]

which is an implicit relation between the zeta potential, the equilibrium rate constants and the saturation surface densities. An explicit solution...
can be found for small zeta potentials ($\zeta \ll kT/\sqrt{qz}$) as

$$\zeta \approx \frac{kT}{qz} \frac{K_+ \sigma_+^e - K_- \sigma_-^e}{1 + K_+ \sigma_+^e - K_- \sigma_-^e} \frac{1}{(1 + K_+ \sigma_+^e)^2} + \frac{1}{(1 + K_- \sigma_-^e)^2}$$  \hspace{1cm} (45)

As an example, consider $\sigma_\pm^e = \sigma_\mp^e$ so that the positive and negative saturation surface densities are equal. If $K_+ = K_-$ neither charged species is preferentially absorbed and $\zeta = 0$. If there is a preferential adsorption of the positive charged carrier then $K_+ > K_-$ and $\zeta > 0$. If the negative charge carrier is preferentially adsorbed, then $K_+ < K_-$ and $\zeta < 0$. This can be simplified further when the density of occupied sites is small compared to the available number sites. Typically the number density of filled sites is much smaller than the saturation density ($\sigma_\pm^e \ll \sigma_\pm^n$). This indicates that the number density $\sigma_\pm^u$ of vacant sites is essentially constant and $K_\pm n_\pm^o \ll 1$ so that Equation (45) reduces to

$$\zeta \approx \frac{kT}{qz} \frac{K_+ - K_-}{2 + K_+ + K_-}$$  \hspace{1cm} (46)

with $K_\pm^+ \equiv K_\pm \sigma_\pm^e/k$ defined as modified equilibrium rate constants. This expression clearly illustrates the role of the rate constants in determining the zeta potential.

### 3.1.2. NON-EQUILIBRIUM CASE

For electrification the dynamic or kinetic description of the interface must be specified. Using the fluxes for the positive and negative carriers in Equations (22) and (23) and the assumption that the surface sites are essentially empty ($\sigma_\pm^n \gg \sigma_\pm^u$, $\sigma_\mp^n \gg \sigma_\mp^u$), the current density at the interface is given by

$$\vec{n}_s \cdot \vec{J} = qz \left[ k_+ \sigma_+^u n_+^o - k_+ \sigma_+^u n_+^o - k_- \sigma_-^u n_-^o + k_- \sigma_-^u n_-^o \right]$$  \hspace{1cm} (47)

Note that $k_\pm$ has units of $[m^3 s^{-1}]$ while $k_\pm^e$ has units of $[s^{-1}]$. Assuming that the effective reaction rates for the charged carriers are not too different so that

$$k_+ \sigma_+^e \approx k_- \sigma_-^e + dk_+$$  \hspace{1cm} (48)

$$k_- \sigma_-^e \approx k_+ \sigma_+^e + dk_-$$  \hspace{1cm} (49)

the interfacial current density can then be expressed as

$$\vec{n}_s \cdot \vec{J} = k_+ \rho^b - k_+ \sigma_+^u + qz \left[ dk_+ \left( n_+^o + n_-^o \right) - dk_- \left( \sigma_+^u + \sigma_-^u \right) \right]$$  \hspace{1cm} (50)

Here $k_\pm$ has units of $[m s^{-1}]$ while $k_\pm^e$ still has units of $[s^{-1}]$. For small perturbations away from equilibrium the last term on the right side (in square brackets) will be essentially constant. Then the current density can be expressed as

$$\vec{n}_s \cdot \vec{J} = k_\pm \rho^b - k_\mp \sigma_+^u - k_\mp \sigma_-^u$$  \hspace{1cm} (51)

with $\xi$ a constant having the units of a volume charge density and caused by the difference in reaction rates between the positive and negative charged carriers. To illustrate the role of $\xi$ consider the equilibrium case of $\vec{n}_s \cdot \vec{J} = 0$ so that

$$\xi = \rho^b/e = \frac{k_+}{k_+} \sigma_+^u$$  \hspace{1cm} (52)

where the superscript $e$ denotes equilibrium. Substituting for the equilibrium volume and surface charge densities in terms of the zeta potential (Equations (30) to (32) and (37)) then gives

$$\xi = -qz n_0 \left[ \frac{2}{kT} \sinh \left( \frac{qz \zeta}{2kT} \right) + \sinh \left( \frac{qz \zeta}{kT} \right) \right]$$  \hspace{1cm} (53)

with $K^e \equiv k_\pm^e/(\lambda k^e)$. This can be simplified for small zeta potentials. With the zeta potential related to the reaction rates through Equation (46) and with the modified reaction rates approximated by

$$K_\pm^e \equiv \frac{k_\pm^e \sigma_\pm^e}{k_\pm^e} \approx K_\pm \left[ 1 \pm \left( \frac{dk_\pm}{k_\pm} - \frac{dk_\mp}{k_\mp} \right) \right]$$  \hspace{1cm} (54)

it follows that

$$\zeta \approx qz n_0 \left( 1 + K^e \right) \left( \frac{dk_\pm}{k_\pm} - \frac{dk_\mp}{k_\mp} \right)$$  \hspace{1cm} (55)

and

$$\xi \approx -qz n_0 \left( 1 + K^e \right) \left( \frac{dk_\pm}{k_\pm} - \frac{dk_\mp}{k_\mp} \right)$$  \hspace{1cm} (56)

The rightmost term in parenthesis gives the difference in reaction rates between the carriers. If there is no difference, $\zeta$ and $\xi$ go to zero. Also, $\zeta$ and $\xi$ have opposite polarities so that $\zeta > 0$ and $\xi < 0$ when positive ions are preferentially adsorbed but $\zeta < 0$ and $\xi > 0$ when negative ions are preferentially adsorbed. From this analysis, it is clear that $\xi$ plays a role similar to $\rho^o$ in Equation (26). Indeed, with $k^e = 0$ in Equation (51), at equilibrium ($J' = 0$) $\xi = \rho^o$. Since $k^e$ is the desorption rate for ions off of the interface, setting it to zero implies the absence of desorption. When $K^e \ll 1$, Equation (56) shows that $\xi \propto n_0$. With the electrical conductivity of the liquid approximated by $\sigma_\pm \approx qz n_0 (b_\pm + b_\mp)$, it follows that $\xi \propto \sigma_\pm$ if the ion mobilities are constant, consistent with previous analysis [26]. But Equation (56) also predicts that other variations with the liquid conductivity are possible, such as $\xi \propto \sigma_0^{3/2} \propto \sigma_0^{3/2}$ when $K^e \gg 1$ and the ion mobilities are constant.

### 3.2. COUETTE GEOMETRY

Next consider the cylindrical 'Couette' geometry shown in Figure 2 where the gap between the cylinders is filled with a dielectric fluid having a permittivity $\varepsilon_2$ and an ohmic conductivity $\sigma_2$. The cylinders
themselves are considered to be perfectly conducting but may be covered with solid dielectrics. For this analysis, only the inner cylinder may be covered by a solid dielectric of permittivity \( \varepsilon_1 \) and conductivity \( \sigma_1 \). The radius of the inner cylinder is \( R_1 \), but the solid dielectric causes the effective radius of the inner cylinder in contact with the fluid to increase to \( a \). The outer cylinder has an inside radius of \( R_2 \). The inner cylinder is electrically connected to the grounded outer cylinder through a load resistance \( R_L \) and a voltage source \( V_o \). The cylinders are assumed to have a height \( H \), but no variations in the azimuthal or axial directions are considered.

3.2.1. GENERAL CHARGE DENSITY AND ELECTRIC FIELD

In the absence of fluid motion, when the cylinders are stationary, the system will reach an equilibrium state depending upon the chemical kinetics of the ionizable impurities and the electrical forces acting upon these species. For two charged species (such as a positive ion \( A^+ \) and a negative ion \( B^- \)) in a stationary medium, the potential distribution across the oil filled gap will be governed by the Poisson-Boltzmann equation in cylindrical coordinates [27]. For the purposes of this model, it is convenient to develop expressions in terms of measurable quantities such as the net current density \( \textbf{j} \) and volume charge density \( \rho \). Assuming the valencies of the ions are given by \( z_{A^+} = -z_{B^-} = z \), the charge conservation equation is obtained by summing Equation (3) for two carriers and multiplying by \( q \) as

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot \textbf{j} = 0
\]  

(57)

Assuming that the diffusivities of each ion are essentially the same or the concentration of ions are only perturbed from the background concentration, then the net current density is obtained by summing Equation (4) for two carriers and multiplying by \( q \) as

\[
\textbf{j} = -D_m \nabla \rho + \rho \mathbf{v} + \sigma_2 \mathbf{E}
\]

\[
D_m = (D_{A^+} + D_{B^-})/2
\]

\[
\sigma_2 = z q \left( n_{A^+} - n_{B^-} \right)
\]

(58)

where \( D_m \) is a composite molecular diffusivity and \( \sigma_2 \) is the fluid conductivity. As long as the contribution to the conductivity caused by the imbalance of charge carrier densities, as manifested by the net charge density, is small compared to the background conductivity the use of a constant \( \sigma_2 \) is justified. This also requires the applied field to be small compared to the equilibrium field in the double layer [11].

To determine the steady state charge density without any fluid motion, substitute Equation (58) into Equation (57) with \( \mathbf{v} \) set to zero. Using Gauss' law and neglecting any axial or azimuthal variations gives the differential equation for the charge density as

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \rho}{\partial r} \right) - \frac{\rho}{\lambda_D^2} = 0
\]

(59)

where \( \lambda_D \) is the Debye length. Note that this expression for the Debye length is slightly different from that given in Equation (31) because only the net charge density, not two individual charge densities, is being considered. The Debye lengths are equal if \( n_{A^+} = n_{B^-} = n_0 \). This is a form of Bessel's equation having modified Bessel functions of order zero, \( I_0(r/\lambda_D) \) and \( K_0(r/\lambda_D) \), as solutions. A solution for the charge density distribution is given by

\[
\rho(r) = \rho_1 \frac{f(R_2, r)}{f(R_2, a)} + \rho_2 \frac{f(r, a)}{f(R_2, a)}
\]

(60)

and the electric field (using the continuity of the radial current density) can be expressed as

\[
E_r(r) = \begin{cases} 
- \frac{2\pi \sigma_1}{\lambda_D} & R_1 < r < a \\
- \frac{2\pi \sigma_1}{\lambda_D} + \frac{\lambda_D}{2} A & a < r < R_2 \\
A \left[ \rho_2 \frac{g(a, r)}{f(R_2, a)} - \rho_1 \frac{g(R_2, r)}{f(R_2, a)} \right] & r = R_2 
\end{cases}
\]

(61)

where \( I \) is the terminal current, \( \rho_1^b \) is the liquid volume charge density at the inner electrode interface at \( r = a \), \( \rho_2^b \) is the liquid volume charge density at the outer interface at \( r = R_2 \) and

\[
f(\alpha, \beta) \equiv I_0 \left( \frac{\alpha}{\lambda_D} \right) K_0 \left( \frac{\beta}{\lambda_D} \right) - K_0 \left( \frac{\alpha}{\lambda_D} \right) I_0 \left( \frac{\beta}{\lambda_D} \right)
\]

(62)

\[
g(\alpha, \beta) \equiv I_0 \left( \frac{\alpha}{\lambda_D} \right) K_1 \left( \frac{\beta}{\lambda_D} \right) + K_0 \left( \frac{\alpha}{\lambda_D} \right) I_1 \left( \frac{\beta}{\lambda_D} \right)
\]

(63)

In the limit when the Debye length is small compared to the radii of the cylinders \( \lambda_D \ll R_1, a, R_2 \), these functions can be approximated by [17] (Section 2.1.6)

\[
f(\alpha, \beta) \approx \frac{\lambda_D}{\sqrt{\alpha \beta}} \sinh \left( \frac{\alpha - \beta}{\lambda_D} \right)
\]

(64)

\[
g(\alpha, \beta) \approx \frac{\lambda_D}{\sqrt{\alpha \beta}} \cosh \left( \frac{\alpha - \beta}{\lambda_D} \right)
\]

(65)

Note that once the interfacial volume charge densities \( \rho_{1,2}^b \) have been determined the charge density profile is known.

3.2.2. INTERFACIAL CHARGE DENSITIES

To determine the interfacial charge densities, the boundary conditions describing the interfacial charge transfer must be specified. In Section 3.1 the boundary condition was given by Equation (31) which is expressed here as

\[
\tilde{n}_i \cdot \textbf{j}_i = k_i^f \rho_i^b - k_i^r \sigma_{sv,i} - k_i^l \xi_i
\]

(66)

with the subscript \( i = 1 \) denoting the inner interface and the subscript \( i = 2 \) denoting the outer interface. The current densities at the inner and outer interfaces are balanced by the transport of charge through the liquid to the interface as

\[
k_1^f (\rho_1^b - \xi_1) - k_1^r \sigma_{sv,1} = \frac{I}{2\pi H_1}
\]

(67)

\[
k_2^f (\rho_2^b - \xi_2) - k_2^r \sigma_{sv,1} = \frac{I}{2\pi H_2}
\]

(68)

The surface charge densities for the ionic species are related to the electric fields on either side of the interfaces (see Equation (27)) using Equations (60) and (61), substitution into Equations (67) and (68) and then solving for \( \rho_1^b \) and \( \rho_2^b \) gives

\[
\rho_1^b = \frac{K_1^r \xi_1 C_2 + K_2^r \xi_2 C_3 + \frac{I_1}{2\pi H_2} A}{C_1 C_2 - C_2 C_3}
\]

\[
A = \left[ (K_1^r - 1) C_2 + (1 - K_2^r) \frac{\alpha}{R_2} C_3 \right]
\]
This shows that the interfacial volume charge densities vary with the terminal current. The first two terms on the right side give the equilibrium integral of the electric field between the cylinders as the terminal constraints on the voltage between the cylinders (the line integral of the electric field between the cylinders) as

\[ v = V_0 + R_L I = \int_{R_1}^{R_2} E_v dr \]

\[ = \frac{\lambda_D^2}{\varepsilon_2} (\rho_{2v} - \rho_b^i) - \frac{I}{2 \pi H} \frac{\sigma_2}{\sigma_1} \ln \left( \frac{a}{R_1} \right) + \ln \left( \frac{R_2}{a} \right) \quad (72) \]

Substituting for the interfacial volume charge densities (Equations (69) and (70)) and solving for the current \( I \) gives

\[ I = \frac{-2 \pi H \sigma_2 A}{B} \]

\[ A = \left\{ v + \frac{\lambda_D^2}{\varepsilon_2} \left[ K_1^T \xi_1 (C_2 - C_4) - K_2^T \xi_2 (C_1 - C_3) \right] \right\} \]

\[ B = \frac{\sigma_2}{\sigma_1} \left[ \ln \left( \frac{a}{R_1} \right) + \ln \left( \frac{R_2}{a} \right) + 2 \pi H R_L \sigma_2 \right] \]

\[ + \frac{\lambda_D}{R_2} (K_2^T - 1) (C_1 - C_3) + \frac{\lambda_D}{R_2} \left( K_1^T - 1 + \frac{\lambda_D}{R_2} \right) (C_2 - C_4) \]

\[ = \frac{C_1 C_2 - C_3 C_4}{C_1 C_2 - C_3 C_4} \quad (73) \]

This shows that the applied voltage \( V_0 \) can increase or decrease the terminal current and hence the charge density on the liquid side of each interface, depending upon the reaction rates at the interface and the relative relaxation times in the solid and liquid dielectrics. In the limit as \( k_T^i \rightarrow 0 \), which corresponds to an absence of interfacial charge desorption, the reaction rates affect the magnitude, but not the polarity, of the charge density perturbation by the flowing current. For example, a positive applied voltage leads to a decrease in \( \rho_b^i \) as negative charge accumulates to shield the applied field from the bulk of the fluid. At the same time, \( \rho_b^i \) is increased as positive charge accumulates near the outer cylinder interface.

### 3.2.3. EFFECTS OF APPLIED VOLTAGE ON INTERFACIAL CHARGE DENSITIES

For flow electrification, the parameters \( \rho_b^i \) and \( \rho_b^p \) reflect the amount of charge available for entrainment in the fluid flow. Although the fluid flow will affect the interfacial volume charge densities and the charge distribution, the stationary analysis clearly indicates a dependence upon the reaction kinetics, the electrical relaxation times and the external circuit. The dependence of \( \rho_b^i \) and \( \rho_b^p \) on the applied voltage provides insight into the roles of the various parameters.

The interfacial volume charge density variation with the applied voltage can be explored by taking partial derivatives with respect to the applied voltage. For convenience the cylinder radii are assumed to be much larger than the Debye length so the electrical double layers are non-interacting. With \( (R_2 - a) \gg \lambda_D \), the approximate expressions for \( f \) and \( g \) (Equations (64) and (65)) apply. Assuming that the Debye length is small enough compared to the cylinder gap so that the hyperbolic terms are approximately equal, defining \( D_v X \) as the partial derivative of \( X \) with respect to the applied voltage and taking \( R_L \rightarrow 0 \), it follows that

\[ D_v \rho_b^i \approx \frac{\varepsilon_2}{\alpha \lambda_D} \left( \frac{1 - K_1^T - \frac{\tau_1}{\tau_2}}{1 + K_1^T} \right) A \quad (74) \]

\[ D_v \rho_b^p \approx \frac{\varepsilon_2}{R_2 \lambda_D} \left( \frac{K_2^T - 1}{1 + K_2^T} \right) A \quad (75) \]

\[ A = \left[ \ln \left( \frac{R_2}{a} \right) + \frac{\sigma_2}{\sigma_1} \ln \left( \frac{a}{R_1} \right) + \frac{\lambda_D (K_2^T - 1) + \lambda_D (K_1^T + \frac{\tau_1}{\tau_2} - 1)}{R_2 + 1 + K_2^T + \left( 1 + \frac{\tau_1}{\tau_2} \right) A} \right] \quad (76) \]

Since the derivatives with respect to the voltage can be positive or negative, an applied voltage can either increase, decrease, or reverse the polarity of the interfacial volume charge density. Note that the denominators are positive definite since \( \lambda_D \gg a, R_2 \) was assumed.

As an initial case study take \( \tau_1 \rightarrow 0, \sigma_1 \rightarrow \infty \), which is applicable to the case of bare metal electrodes or when the solid dielectric is very conducting with respect to the liquid dielectric. For convenience, assume that the electrodes are the same so that \( K_1^T = K_2^T \equiv K_T^r \) and \( K_1^T = K_2^T \equiv K_m^e \). This then gives

\[ D_v \rho_b^i \approx \frac{-R_2}{a} D_v \rho_b^p \quad (77) \]

\[ \approx \frac{\varepsilon_2}{\alpha \lambda_D} \left[ \frac{(1 - K_m^e)}{(1 + K_m^e) \ln \left( \frac{R_2}{a} \right) - \frac{\lambda_D}{a} (1 + \frac{\tau_1}{\tau_2}) (1 - K_m^e)} \right] \]

This indicates that the polarity of the interfacial charge density variation with the applied voltage depends upon the interfacial reaction rates, with opposite effects always occurring at the inner and outer interfaces. If the left term in the denominator is larger than the right term, the field across the fluid is dominated by the ‘ohmic’ contribution rather than the interfacial charge dynamics and charge diffusion. The polarity is then determined by the quantity \( 1 - K_m^e \), with \( D_v \rho_b^i \) positive for \( K_m^e < 1 \) but negative for \( K_m^e > 1 \). If the left term in the denominator is smaller than the right term, the ohmic contribution to the field is dominated by the interfacial charge dynamics and charge diffusion and \( D_v \rho_b^i \) is always negative. Implicit to this last condition is the constraint of \( K_m^e > 1 \) so that charge relaxation is fast compared to interfacial desorption.

Physically, \( K_m^e = 1/(K_1^T \tau_2) \) describes the competition between charge desorption from the interface and charge relaxation in the liquid.
bulk as the mobile ions redistribute themselves to shield the bulk of the liquid from any applied fields. For $K_m^+ > 1$, the charge desorption is slow compared to charge relaxation and the volume charge density near the inner cylinder interface becomes negative (for positive applied voltages) while near the outer cylinder the charge density becomes positive. This is the heterocharge case because the volume charge on the liquid side of the interface has a polarity opposite that of the surface charge on the interface. For $K_m^- < 1$, charge desorption is fast compared to charge relaxation and the volume charge density near the inner cylinder interface increases while near the outer cylinder the charge density decreases for positive applied voltages. This is the homocharge case because the volume charge density on the liquid side of the interface and the surface charge at the interface have the same polarity. The parameter $K_m^+$ contains the adsorption rate constant and influences whether the 'ohmic' contribution or the reaction dynamics are dominant.

Next, consider the case of a solid dielectric that is very insulating with respect to the fluid ($r_1 \gg r_2$). Once again, the interfacial charge densities depend upon desorption rates at each interface. In the limit that $K_2^+ r_1 > 1$ and $r_1 / r_2 \gg K_2^+$, conduction through the solid is slow compared to the interfacial desorption rates and the interfacial charge density voltage derivatives are given by

$$D_v \rho_i^b \approx -\frac{\varepsilon_i}{a \lambda_D} \left[ K_i^i + 1 \right] \ln \left( \frac{a}{R_i} \right) + \frac{2 \rho_i}{a} \frac{\varepsilon_i}{\varepsilon_2}$$

$$D_v \rho_i^b \approx 0$$

The electric field resulting from the applied voltage is primarily contained inside the solid dielectric and charge accumulates in the double layer at the inner interface to shield the applied field from the fluid volume. As the factor $K_i^i$ increases, adsorption onto the interface increases so that the interfacial surface charge accumulate (becomes more negative) and less charge is necessary in the double layer to shield the applied field. The result is a volume charge density near the interface that decreases in magnitude. The volume charge density near the outer cylinder interface is essentially unaffected because the field is nearly zero there. In the limit that $K_2^+ r_1 < 1$ and $r_1 / r_2 \ll K_2^+$ conduction through the solid is fast compared to the interfacial desorption rates and the interfacial charge density voltage derivatives are given by

$$D_v \rho_i^b \approx -\frac{\varepsilon_i}{a \lambda_D} \times \frac{1}{\frac{a}{R_1} + \frac{2 \rho_i}{a} \frac{K_i^i}{K_i^{i+1}}}$$

$$D_v \rho_i^b \approx 0$$

4. NON-STATIONARY CASE

This Section considers the effects of fluid flow on electrification for the geometry of Figure 2. The motion of the fluid redistributes the chemical species, carrying charge from the double layers at the interfaces into the core region of the fluid flow. This results in a measurable charge density in the volume of the fluid and a terminal current and/or voltage across the electrodes. In this analysis only steady state relations are obtained.

4.1. HYDRODYNAMICS

The fluid motion is created by rotation of the inner cylinder with the outer cylinder kept stationary. This rotation is at speeds that are high enough to provide turbulent mixing, creating a 'core' region where the densities of the species of interest (neutral positive and negative charge carriers) can be taken as essentially uniform. At the edge of this region, near the boundaries, diffusion sublayers develop in which molecular diffusion and drift dominate the convective mixing by the turbulent flow. For the semi-insulating liquids of interest in electrification, the Debye length and the diffusion sublayer thickness are of the same order so both drift and diffusion contribute to the flux of the ions. In contrast, in the relatively conducting aqueous solutions studied in most mass transfer experiments, the Debye length is much smaller than the sublayer thickness and the flux contribution due to drift is negligible compared to diffusion. Including the drift contribution to the flux significantly complicates the model for the mass (and charge) transport; to reduce some of this complexity, the effects of the turbulence on the transport will be represented by a uniform molecular diffusivity in the sublayer region and a turbulent diffusivity outside the sublayer. The price paid for this assumption is that the sublayer thickness must be known accurately.

Rotation of the inner cylinder causes turbulent mixing and charge redistribution, and some of the charge is transported from the electrical double layers into the bulk of the liquid volume. For semi-insulating oils, the turbulent mixing creates a core region where the charge density can be taken as essentially uniform. At the edge of this region, diffusion sublayers develop in which molecular diffusion and drift dominates the convective mixing by turbulent flow. Typically the thickness of the sublayer is taken as the distance where the molecular and turbulent diffusivities are equal. Empirical fluid mechanical studies show that the sublayer thickness is inversely proportional to the square root of the wall shear stress at each interface so that a balance of torques yields the sublayer thickness $\delta_1$ at the inner cylinder and $\delta_2$ at the outer cylinder as [11, 28]

$$\delta \equiv \frac{\delta_1}{a} = \frac{\delta_2}{R_2} \equiv \frac{3.3}{S_c^{0.356} R_e C_f}$$

with $\delta$ a normalized sublayer thickness, $R_e \equiv 2 \Omega a^3 / \nu$ the Reynolds number, $\Omega$ the inner cylinder angular velocity (rad/sec), $\nu$ the kinematic viscosity of the fluid, $S_c \equiv \nu / D_m$, the Schmidt number, $D_m$ the molecular diffusivity, and $C_f$ the drag coefficient, given by

$$\frac{1}{C_f} \approx -0.6 - 4.07 \log_{10} \left( \frac{2}{R_e C_f} + 0.215 \frac{e}{\delta} \right)$$

$$8 \times 10^2 < R_e < 8 \times 10^6$$

where $e$ is the surface roughness height [29]. As the rotation rate increases, $R_e$ increases but the diffusion sublayer thickness decreases. At
high enough \( R_e, C_f \) becomes independent of \( R_e \) and depends only upon the surface roughness.

While these relations were determined for relatively low Schmidt number fluids (\( 10^3 < S_c < 10^5 \)) [30], they are also applied to higher Schmidt number fluids such as transformer oil (\( 10^4 < S_c < 10^6 \)). Other relations for the drag coefficient have also been used but these tend to overestimate the sublayer thickness and require larger than expected molecular diffusivities or shear stresses to fit the data [28, 30]. In addition surface roughness may play a role in enhancing the molecular diffusivity; it has been observed to greatly increase the mass transfer once a critical Reynolds number has been attained [30, 32]. Physically, the surface roughness increases the drag coefficient and decreases the sublayer thickness. Smooth cylinder expressions then overestimate the sublayer thickness. In the experimental Couette apparatus, the stainless steel metal surfaces are relatively smooth but contain numerous feed-throughs for instrument probes and the calendered dielectric surfaces are known to have roughness and periodicities that are comparable to or larger than the diffusion sublayer thickness [33]. Despite these shortcomings, these relations provide a good first-order estimate of the hydrodynamic sublayer thickness.

### 4.2. BASIC SOLUTION

With several assumptions, general relations between the measurable quantities (volume charge density in the core region, terminal current, terminal voltage, and the rate of change in the core charge density with respect to an imposed dc terminal voltage) and the interfacial and bulk parameters are derived. It is assumed that the turbulent mixing causes the species densities to be independent of the axial and azimuthal directions and approximately uniform in the core region. In terms of the net charge density, a uniform charge density across the core region occurs when the turbulent Debye length, based upon the turbulent diffusivity instead of the molecular diffusivity, is large compared to the annular gap. Quasi-unipolar species are considered so that only the net charge density and net current density must be determined, not the individual carrier dynamics associated with two (or more) charged species. As in the stationary case, the carrier densities near the solid/liquid interfaces are assumed to be similar to the bulk densities so that a region of enhanced conductivity near the interfaces does not have to be modeled. This is tantamount to assuming small interfacial zeta potentials and applied voltages so that the conduction through the liquid can be represented by the bulk ohmic conductivity [11].

While the turbulent mixing creates a uniform charge density in the core region, the sublayer regions are not well-mixed and the charge density will vary in the radial direction. The governing equation for this distribution in the sublayer is still Equation (59) because the mean convection velocity is in the azimuthal direction and only variations in radius \( r \) are considered. It follows that the charge distribution can be expressed as

\[
\rho(r) = \begin{cases} 
0 & (I) \quad R_1 < r < a \\
\rho_f f(a + \delta_1, r) + \rho_i f(r, a) & (II) \quad a < r < a + \delta_1 \\
\rho_o f(R_2 - \delta_2, r) + \rho_f f(r, R_2 - \delta_2) & (III) \quad a + \delta_1 < r < R_2 - \delta_2 \\
\rho_o f(R_2, r) + \rho_f f(r, R_2 - \delta_2) & (IV) \quad R_2 - \delta_2 < r < R_2 
\end{cases}
\]

(82)

where \( \rho(r) \) is the radially dependent volume charge density, \( \rho_o \) is the uniform charge density in the turbulent core region and the charge densities on the liquid side of the solid/liquid interface are given by \( \rho_f \) for the inner cylinder interface and \( \rho_f^{b} \) for the outer cylinder interface. The roman numerals are used to identify the regions of applicability for each expression. This distribution is shown schematically in Figure 3. The electric field distribution corresponding to this charge distribution can be obtained from the differential form of Gauss' law and integrating over the radial coordinate to give

\[
E_r(r) = \begin{cases} 
-\frac{1}{2\pi\epsilon_0 R_1} & (I) \\
-\frac{1}{2\pi\epsilon_0 R_1} + \frac{\lambda_D}{\epsilon_0 f(a + \delta_1, a)} & (II) \\
-\frac{1}{2\pi\epsilon_0 R_2} + \frac{\lambda_D}{\epsilon_0 f(R_2 - \delta_2, R_2 - \delta_2)} & (III) \\
-\frac{1}{2\pi\epsilon_0 R_2} + \frac{\lambda_D}{\epsilon_0 f(R_2, R_2 - \delta_2)} & (IV) 
\end{cases}
\]

(83)

with \( A_3 \) an integration constant to be determined from the boundary conditions. This steady state expression for the electric field satisfies the required continuity of the radial current density. The integration constant \( A_3 \) results from the turbulent diffusivity being taken as infinite in the core region so that the gradient in the charge density is zero and the product of the diffusivity and charge density gradient is a finite quantity.

In addition the electric field must be continuous across the fluid volume because the dielectric permittivity is constant. Continuity of the electric field at the interfaces between the sublayer and core regions \((r = a + \delta_1 \text{ and } r = R_2 - \delta_2)\) with Equation (83) gives

\[
\frac{A_3}{(a + \delta_1)} + \frac{\rho_o(a + \delta_1)}{2\epsilon_2} = \frac{\lambda_D}{\epsilon_2} \times 
\frac{[\rho_o g(a + \delta_1, a) - \rho_f g(a + \delta_1, a + \delta_1)]}{f(a + \delta_1, a)}
\]

(84)
\[
\frac{A_3}{(R_2 - \delta_2)} + \frac{\rho_o(R_2 - \delta_2)}{2\varepsilon_2} = \lambda_D \times \frac{[p_2^2 g(R_2 - \delta_2, R_2 - \delta_2) - \rho_o g(R_2, R_2 - \delta_2)]}{f(R_2, R_2 - \delta_2)}
\]

Taking the line integral of the radial component of the electric field between the electrodes gives

\[
v = V_o + R_L I = \int_{R_1}^{R_2} E \cdot dr = -\frac{I}{2\pi \varepsilon_2 \sigma_0} \left[ \ln \left( \frac{a}{R_1} \right) + \ln \left( \frac{R_2}{a} \right) \right] + A_3 \ln \left( \frac{R_2 - \delta_2}{a + \delta_2} \right) + \frac{\rho_o}{4\varepsilon_2} \left[ (R_2 - \delta_2)^2 - (a + \delta_1)^2 \right] + \frac{\lambda_D^2}{\varepsilon_2} (p_2^b - p_1^b)
\]

Note that the terminal voltage \(v\) can be obtained from the terminal current \(I\) after the current is found.

These general expressions can be simplified further when the cylinder radii are large compared to the sublayer thicknesses and the Debye length. For example, in the Couette apparatus experiments of [10] the cylinder radii scale as \(a/R_2 \approx 1\), the non-dimensional sublayer thickness scales as \(\delta \ll 1\), and the Debye length is small compared to the cylinder radii \(\lambda_D/R_2 \ll 1\). This allows the approximate expressions for \(f\) (Equation (64)) and \(g\) (Equation (65)) to be used. Furthermore, the sublayer thicknesses can be assumed to have values that are limited on the upper side by the Debye length \(\delta \ll \lambda_D/R_2\) and on the lower side by \(\delta \gg (\lambda_D/R_2)^2\). After eliminating \(A_3\) using Equations (84) to (86), non-dimensionalizing according to Tables 1 and 2, and applying the boundary conditions for the interfacial charge transfer (to be described in more detail in the following sections), the governing equations for the measurable quantities can be written as

\[
g_{oc}^c \lambda_D = \left\{ P_1 \left[ \frac{1}{2} + \frac{\ln(a)}{1 - a^2} \right] + P_2 \left[ \frac{1}{2} + a^2 \frac{\ln(a)}{1 - a^2} \right] \right\}
\]

for the open-circuit voltage \((I = 0, R_L \rightarrow \infty)\),

\[
\frac{\rho_o}{\lambda_D} = \frac{2}{(1 - a^2)} \left[ P_1 + P_2 \right]
\]

for the open-circuit charge density,

\[
I_{oc}^c = \frac{2}{\gamma_0} g_{oc}^c
\]

\[
\gamma_0 = \frac{1}{\sigma_1} \ln \left( \frac{a}{R_1} \right) - \ln(a) - P_3 \left[ \frac{1}{2} + \frac{\ln(a)}{1 - a^2} \right] + P_4 \left[ \frac{1}{2} + a^2 \frac{\ln(a)}{1 - a^2} \right]
\]

for the short-circuit current \((v = 0, R_L \rightarrow 0)\),

\[
\frac{\rho_o}{\lambda_D} = \frac{g_{oc}^c}{\lambda_D} + \frac{1}{(1 - a^2)} \left[ P_3 - P_4 \right] g_{sc}^c \lambda_D
\]

for the short-circuit charge density, and

\[
\frac{D_o \phi}{\lambda_D} = \frac{2}{(1 - a^2)} \gamma_0 \left( P_4 - P_3 \right) = \frac{\rho_o - \rho_o^{oc}}{V_o - \phi^{oc}}
\]

for the rate of change of the charge density with applied voltage. The rightmost expression indicates that \(D_o \phi\) can be determined from open-circuit and short-circuit measurements with \(V_o = 0\). The underscore beneath a variable indicates that it is normalized. Note that the normalization for the current in Table 1 yields the conventional mass transfer parameter, the Sherwood number. Since the resistance normalization includes a factor of 2, the normalized terminal voltage is expressed as

\[
v = \frac{\gamma_0 V_o + R_L v_{oc}}{R_L + \gamma_0}
\]

(93)

\[
I = \frac{2}{R_L + \gamma_0} (v_{oc} - V_o)
\]

(94)

While it is mathematically possible for \(\gamma_0\) to be negative so that the quantity \(R_L + \gamma_0\) is zero, no physical mechanisms leading to an ‘infinite’ voltage or current are evident. By constraining \(\gamma_0 > 0\), the voltage and current can be kept finite, independent of the terminal connections. This constraint is guaranteed to be satisfied if each of the individual terms in \(\gamma_0\) are positive, which in turn imposes constraints on the effective reaction rate constants.

### Table 1. Normalizations for the electrification model variables.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Normalization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lengths</td>
<td>((x, y, z) \rightarrow (x, y, z) R_2)</td>
</tr>
<tr>
<td>Charge density</td>
<td>(\rho_o^l = \rho_o^l \sigma_o/b)</td>
</tr>
<tr>
<td>Electric potential</td>
<td>(v = V_D m/b)</td>
</tr>
<tr>
<td>Terminal resistance</td>
<td>(R_L = R_L/2\pi H \sigma_o)</td>
</tr>
<tr>
<td>Terminal current</td>
<td>(I = I_R H \sigma_o D_m/b)</td>
</tr>
<tr>
<td>Terminal voltage</td>
<td>(V_o = V_o D_m/b)</td>
</tr>
<tr>
<td>Solid conductivity</td>
<td>(\sigma_1 = \sigma_1 \sigma_o)</td>
</tr>
<tr>
<td>Solid relaxation time</td>
<td>(\tau_1 = \tau_1 \tau_o)</td>
</tr>
<tr>
<td>Reaction velocity</td>
<td>(k_i = k_i D_m/R_2)</td>
</tr>
<tr>
<td>Charge density gradient</td>
<td>(\alpha_i = \alpha_i \sigma_o/b R_2)</td>
</tr>
<tr>
<td>Effective charge density</td>
<td>(\xi_i = \xi_i \sigma_o/b)</td>
</tr>
</tbody>
</table>

### Table 2. Summary of parameters used in the electrification model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sublayer thickness</td>
<td>(\delta = \delta_1/a = \delta_2/R_2)</td>
</tr>
<tr>
<td>Liquid relaxation time</td>
<td>(\tau_0 = \varepsilon_0/a)</td>
</tr>
<tr>
<td>Solid relaxation time</td>
<td>(\tau_1 = \varepsilon_1/\sigma_1)</td>
</tr>
<tr>
<td>Debye length</td>
<td>(\lambda_D = \sqrt{D_m \tau_0})</td>
</tr>
<tr>
<td>Rate constant</td>
<td>(k_i = k_i D_m r_i)</td>
</tr>
<tr>
<td>Reverse reaction rate</td>
<td>(K_i = 1/\tau_2 k_i^r)</td>
</tr>
</tbody>
</table>
4.3. CHEMICAL REACTION BOUNDARY CONDITION

With the free surface charge density at each solid/liquid interface determined by the electric field (of Equations (27) and (83)) as

\[ \sigma_{\text{sn1}} = \lambda_D \left[ -\rho_o \frac{g(a + \delta_1, a)}{f(a + \delta_1, a)} + \rho_o \frac{g(a, a)}{f(a + \delta_1, a)} \right] \]

\[ + \left( \frac{\varepsilon_2}{\sigma_2} - \frac{\varepsilon_1}{\sigma_1} \right) \frac{I}{2 \pi H a} \] (95)

\[ \sigma_{\text{sn2}} = -\lambda_D \left[ -\rho_o \frac{g(R_2, R_2)}{f(R_2, R_2 - \delta_2)} \right. \]

\[ + \left. \frac{\rho_o}{f(R_2, R_2 - \delta_2)} \right] \varepsilon_2 \frac{I}{2 \pi H R_2} \] (96)

the boundary conditions of Equation (66) at each solid/liquid interface become

\[ p_1^b \left[ f^\epsilon_1 + \frac{g(a + \delta_1, a)}{f(a + \delta_1, a)} \right] - \rho_o \frac{g(a, a)}{f(a + \delta_1, a)} \]

\[ - \frac{I \tau_1}{2 \pi H \lambda_D a} \left( K^\eps_1 - 1 + \tau_1 \right) = K^\eps_1 \varepsilon_1 \] (97)

\[ p_2^b \left[ f^\epsilon_2 + \frac{g(R_2, R_2 - \delta_2)}{f(R_2, R_2 - \delta_2)} \right] - \rho_o \frac{g(R_2, R_2)}{f(R_2, R_2 - \delta_2)} \]

\[ - \frac{I \tau_2}{2 \pi H R_2} (1 - K^\eps_2) = K^\eps_2 \varepsilon_2 \] (98)

When the cylinder radii are large compared to the sublayer thickness and the Debye length, combining these relations with Equations (84) to (86) and non-dimensionalizing according to Tables 1 and 2 then gives coefficients for Equations (87) to (92)

\[ P_1 = \frac{a^2}{\sinh \left( \frac{a}{\lambda_D} + \frac{\varepsilon_1}{\lambda_D} \right)} \] (99)

\[ P_2 = \frac{\varepsilon_2}{\sinh \left( \frac{a}{\lambda_D} + \frac{\varepsilon_2}{\lambda_D} \right)} \] (100)

\[ P_3 = \frac{K^\eps_2 (K^\eps_1 + \tau_1 - 1)}{\sinh \left( \frac{a}{\lambda_D} + \frac{1}{\lambda_D} \right)} \] (101)

\[ P_4 = \frac{K^\eps_2 - 1}{\sinh \left( \frac{a}{\lambda_D} + \frac{1}{\lambda_D} \right)} \] (102)

which are summarized as case 3 in Table 3. Some aspects of this model can be explored through limiting cases.

Consider first identical bare metal electrodes with interfacial parameters \( K^\eps_1 = K^\eps_2, K^\eps_1 = K^\eps_2 \), and \( \varepsilon_1 = \varepsilon_2 \). The effects of these parameters can be explored by fixing two of them and letting the third vary. For example, consider Figure 4 in which \( K^\eps_1 \) is varied for a given \( K^\eps_2 \) and \( \varepsilon_{1,2} \), whose values were chosen to give magnitudes that are comparable to those observed in the experiments. This Figure shows that the open-circuit voltage is independent of \( K^\eps_1 \) (Equation (87)) and the sublayer thickness \( (\delta / \lambda_D \sim 0.3) \) that led to an open-circuit voltage of zero also led to a short-circuit current of zero, independent of \( K^\eps_1 \) (Equation (89)). While \( \rho_o^\text{oc} \) is also independent of \( K^\eps_1 \) (Equation (88)), \( \rho_o^\text{oc} \) is seen to be only weakly dependent on \( K^\eps_1 \) (Equation (91)). In contrast, the short-circuit current and \( D_o^\text{p} \) depend strongly on \( K^\eps_1 \). In particular, for \( K^\eps_1 < 1, D_o^\text{p} > 0 \), but for \( K^\eps_1 > 1, D_o^\text{p} < 0 \). Also note that the terminal quantities (voltage and current) have polarity changes that are dependent only upon the rotation rate which controls \( \delta \). This is reasonable because the terminal quantities depend upon the difference in effects occurring at each interface and would be zero for a parallel plate geometry. Since the interfaces are curved in this system, the sublayer thicknesses are different at each interface and small changes in the thickness of the sublayer, relative to the Debye length, have significant effects on the terminal quantities.

The strong electrification dependence on \( K^\eps_1 \) is shown in Figure 5, where \( K^\eps_1 \) and \( \varepsilon_{1,2} \) are fixed and \( K^\eps_2 \) is varied. For \( K^\eps_1 \) large, the reaction rates are fast, the charge densities have a polarity opposite that of the terminal quantities and the voltage and current are proportional to each other. This matches the predictions of the "constant wall charge density" model [28]. As \( K^\eps_1 \) becomes smaller, the polarity of the terminal quantities depends upon the sublayer thickness and the voltage and current are no longer linearly related to one another. \( D_o^\text{p} \) is always positive in this example because \( K^\eps_1 < 1 \). If \( K^\eps_1 > 1, D_o^\text{p} \) is always negative. If \( K^\eps_1 = 0 \), the open and short-circuit charge densities are equal and \( D_o^\text{p} = 0 \). The magnitude of \( \varepsilon_{1,2} \) affects the scaling of the charge density, the open-circuit voltage and the short-circuit current, similar to \( K^\eps_1 \), but does not affect \( D_o^\text{p} \).

In most situations, the interfaces are not identical. Occasionally this
Table 3. Limiting cases for the parameter estimation of $P_i$ in the electrification model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limiting Cases</th>
<th>Limiting Cases</th>
<th>Limiting Cases</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_1$</td>
<td>$\frac{\kappa_1^{2} K_1^{2}}{\sinh(\frac{a}{2D})}$</td>
<td>$\frac{\kappa_1^{2} K_1^{2}}{\cosh(\frac{a}{2D})}$</td>
<td>$\frac{\kappa_1^{2} K_1^{2}}{\sinh(\frac{a}{2D})}$</td>
</tr>
<tr>
<td>$P_2$</td>
<td>$\frac{1}{2D} \sinh(\frac{a}{2D})$</td>
<td>$\frac{1}{2D} \sinh(\frac{a}{2D})$</td>
<td>$\frac{1}{2D} \sinh(\frac{a}{2D})$</td>
</tr>
<tr>
<td>$P_3$</td>
<td>$\frac{1}{2D} \sinh(\frac{a}{2D})$</td>
<td>$\frac{1}{2D} \sinh(\frac{a}{2D})$</td>
<td>$\frac{1}{2D} \sinh(\frac{a}{2D})$</td>
</tr>
<tr>
<td>$P_4$</td>
<td>$\frac{1}{2D} \sinh(\frac{a}{2D})$</td>
<td>$\frac{1}{2D} \sinh(\frac{a}{2D})$</td>
<td>$\frac{1}{2D} \sinh(\frac{a}{2D})$</td>
</tr>
</tbody>
</table>

Figure 5. Normalized calculated response for identical bare metal cylinders with $K_1^{2}$ varied and $\kappa = a/R_2 = 0.75$. Both the open-circuit and short-circuit charge densities are plotted and are essentially identical. For $K_1^{2}$ large, the results of the model using the generalized Abedian-Sonin boundary condition are obtained.

Figure 6. Normalized calculated response for bare metal cylinders with $\kappa^2 = \xi_2^2 \omega_2^2 / b$ and $K_1^{2}$ varied and $\kappa = a / R_2 = 0.75$. While the open-circuit charge density (solid line) is independent of $K_1^{2}$, the short-circuit charge density dependence on $K_1^{2}$ is indicated by the dashed lines.

is intentional, such as when copper or pressboard is used to cover the inner cylinder. Other times it is unintentional, such as when the cylinders are both bare stainless steel but the cleaning of the cylinders or the past history of an experiment causes the interfaces to be slightly different. For $K_1^{2}$ large, the results of the model using the generalized Abedian-Sonin boundary condition are obtained.

Relative variations in $K_1^{2}$ lead to similar results for the charge density, voltage and current, as shown in Figure 7. The similarity of these results leads to difficulties in experimentally differentiating between the effects of variations in $K_1^{2}$ and $\xi_2^2$. For example, when $K_1^{2} \gg 1$, the polarity of the voltage and the current are not as sensitive to the relative values of the $K_1^{2}$ on the inner and outer interfaces and variations in the polarity of the terminal quantities are usually estimated as relative differences in the $\xi_2^2$. When $K_1^{2} \ll 1$, the product $\xi_2^2 K_1^{2}$ at each interface becomes important and the two parameters are not easily separated. In contrast to Figure 6, $D_\alpha \rho_\alpha$ is strongly affected by the $K_1^{2}$ variation which suggests that it can be used to estimate the $K_1^{2}$. Unfortunately, the measurement of $D_\alpha \rho_\alpha$ is more prone to error than the
other electrification quantities.

In Figure 8, the effects of an insulating dielectric layer on the inner cylinder are explored. It was assumed that the interfacial parameters were the same at the inner and outer interfaces and the relative conductivity (and relaxation time) of the solid was varied. As expected from Equations (87) and (88), the solid conductivity does not affect the open-circuit voltage or the open-circuit charge density. While the short-circuit charge density is only slightly affected by the decreasing conductivity via $L_s$, the magnitude of the current decreases strongly with the decreasing conductivity via $y_o$. $D_s p_o$ is negative, similar to the $K_i^r = 1$ and $K_i = 0.5$ case because $\tau_i$ acts to increase the effective $K_i$. As the solid becomes more insulating, $L_s$ decreases, as expected, but $D_s p_o$ increases, indicating that a given applied voltage will lead to larger $\chi_s$. In actual transformers where the solid is a pressboard insulation, under dry conditions the pressboard may become insulating enough to lead to these enhanced charge densities due to the dc fields from the electrification process itself.

4.4. IMPOSED INTERFACIAL CURRENT DENSITY

The Abedian-Sonin boundary condition proposes that the current densities at the interfaces are given by Equation (26). Although Abedian and Sonin further restricted themselves to infinite reaction velocities ($k_o \to \infty$) so that $\rho^b = \rho^w$, finite $k_o$ are considered here. The coefficients for Equations (87) to (92) then become

\[ P_1 = \frac{\alpha p^w}{\sinh \left( \frac{\alpha b}{\lambda_D} \right)} \]  
\[ P_2 = \frac{\rho^w}{\sinh \left( \frac{b}{\lambda_D} \right)} \]  
\[ P_3 = \frac{1}{k_1 \lambda_D \sinh \left( \frac{\alpha b}{\lambda_D} \right)} \]  
\[ P_4 = \frac{1}{k_2 \lambda_D \sinh \left( \frac{b}{\lambda_D} \right)} \]

Since this boundary condition is the limiting case of Equation (66) obtained when $k_i^r = 0$, it follows that $k_i = k_i^f$ and $\rho_i^w = \chi_i$. This is summarized in case 1 of Table 3.

Representative plots of the open-circuit core charge density and voltage are given in Figure 9. Under open-circuit conditions, the charge density and voltage are independent of the reaction velocities and increase in magnitude as the rotation rate of the inner cylinder increases and the sublayer thickness decreases. Physically, as the sublayer thickness decreases relative to the Debye length, an increasing portion of the charge in the electrical double layers is swept into the turbulent core region. The polarity of the voltage, relative to that of the charge density,
wall charge density at the outer cylinder is slightly larger than that at the interface is equal to or smaller than the wall charge density on the inner cylinders, which is proportional to the open-circuit voltage, is also plotted. But if the wall charge density on the outer cylinder is much larger than that on the inner cylinder, they have the same polarity. In the intermediate regime (determined by the value of $p^-_0/p^a$), the charge density and voltage have the opposite polarity. Similar results can be obtained when they have opposite polarities; if the inner and outer cylinders were assumed to have the same polarity. While several inconsistencies in the derivation of the boundary condition (including the inconsistent use of transference numbers, an interfacial current density that must be zero in a system containing two solid/liquid interfaces, and a double counting of the ohmic contribution to the current) limit the physical interpretation that can be attributed to this boundary condition, the general form of the boundary condition in terms of the constants $\alpha_0$ gives results similar to the previously discussed boundary conditions. Indeed, solving for the coefficients $P_i$ yields

$$P_1 = \frac{a\alpha_0 \lambda_D}{\cosh (a\beta)}$$

and $P_3 = P_4 = 0$. The parameters $P_1$ and $P_2$ follow from the $K_i^+ \gg 1$ limiting case of Equations (99) to (102), summarized in case 2 of Table 3, with $\alpha_0 = \ell_2 K_i^+ / \lambda_D$. This implies that the open and short-circuit charge densities are always equal and independent of the applied voltage. In addition, the ratio of the short-circuit current to the open-circuit voltage ($\gamma_0$) is a constant, independent of the flow rate.

## 5. COMPARISON TO EXPERIMENTS

In this Section several sets of experimental measurements, described in [10, 11], are used to estimate the values of the interfacial parameters.

### 5.1. PARAMETER ESTIMATION APPROACH

In order to compare the model to the experimental data, the kinematic viscosity of the oil and the molecular diffusivity of the charged species must be known as a function of temperature ($T$ in K). For this work, the kinematic viscosity $\nu$ of the oil is assumed to be given by

$$\nu = \nu_0 \exp\left[\frac{W_o}{kT}\right]$$

where $k = 8.6167 \times 10^{-5}$ eV/K is Boltzmann's constant, $\nu_0 = 3.95 \times 10^{-10}$ m$^2$/s and $W_o = 0.2725$ eV [36]. Since the ionic species are not known, the ionic diffusivity must be estimated. Empirically, the ion mobility $b$ (m$^2$/Vs) in hydrocarbon liquids is related to the viscosity $\eta$ (kg/ms) by Walden's rule as [37]

$$b \eta \approx 2 \times 10^{-11}$$

in C/m with $\eta = P_m \nu$ the dynamic viscosity of the liquid and $P_m \approx 886$ kg/m$^3$ the oil mass density [38]. The molecular diffusivity $D_m$ can then be obtained from Einstein's relation (Equation (5) with $z = 1$). Thus, the temperature sets the viscosity of the oil and the ionic diffusivity can be estimated from the calculated mobility and the Einstein relation. For the experiments, the diffusion sublayer thicknesses and Debye
lengths are estimated to be roughly the same, varying to ~50 μm. In terms of the normalized variables, \( \delta \approx \lambda_{DD} \).

The complicated nature of the estimation, where multiple parameters (\( \xi_0, K^e, \) and \( K^r \) at each interface) are used to fit several types of measurements (charge density and terminal data), required a two-step approach. The first step was to invert Equations (87) and (88) for the open-circuit measurements as

\[
P_1 = \frac{\nu^{\text{OC}}D_{DD}}{\ln(\delta)} - \frac{1}{2} \frac{D_{\nu^{\text{OC}}}}{\lambda_{DD}} \left[ a^2 + \frac{(1 - a^2)}{2 \ln(\delta)} \right]
\]

so that \( P_1 \) and \( P_2 \) were calculated at each flow rate or sublayer thickness. The parameters \( \xi_0 \) and \( K^e \) were then estimated from a least-squares fit using each of the three cases defined in Table 3. The fit that led to the smallest 'goodness-of-fit' number \( \chi^2 \), defined by

\[
\chi^2 = \sum_{n=1}^{N} \left( \frac{P_{\text{meas}} - P_{\text{cal}}}{P_{\text{cal}}} \right)^2
\]

for \( N \) data points, was then denoted as the best case for each interface. When the goodness-of-fit number was similar between the general case (3) and either of the limiting cases (1 or 2), the limiting case was taken as the best case because that estimation required fewer free variables.

The second step in this approach was to invert Equations (89) and (91) for the short-circuit measurements as

\[
P_3 = -1 + \frac{\ln \left( \frac{\delta}{\lambda_{DD}} \right)}{a_1 \ln(\delta)}
\]

so that \( P_3 \) and \( P_4 \) were calculated at each flow rate. With the case determined from the open-circuit measurements, the remaining unknowns were estimated from a least-squares fit to the \( P_3 \) and \( P_4 \) data. In this approach it was assumed that the open-circuit data is more accurate, at least in determining the appropriate case for each interface, because it is independent of the conduction through the interface and the dielectric materials.

5.2. PARAMETER ESTIMATION RESULTS

Representative plots of the normalized electrification data are given in Figure 10 for bare metal cylinders and in Figure 11 for pressboard insulation covering the inner cylinder. The plots on the left side of each Figure show the electrification data plotted against the Reynolds number and the plots on the right side show the same data plotted against the ratio of the diffusion sublayer thickness to the Debye length, using the correlation of Equations (80) and (81). The critical parameter for the electrification is not simply the Reynolds number but the relative thickness of the sublayer to the Debye length. These Figures clearly show the increase in electrification that occurs once the sublayer thickness becomes smaller than the Debye length.

The lines in both Figures were obtained from the model after estimating the values of the interfacial parameters. When applying this estimation routine to the experimental data, the model incorporating the generalized Abedian-Sonin boundary condition (limiting case 1 of Table 3) usually gave the best fit to the data. A good fit was obtained for the charge density and voltage, but the fit to the current and \( I_{DC} \) was relatively poor due to the nature of the measurements and the estimation. A representative plot of the measured and estimated values of the \( P_i \) is given in Figure 12. There is relatively good agreement between the measured and fit values. The large variation in the measured values of \( P_3 \) and \( P_4 \) is indicative of the uncertainty in the measurements of \( I_{DC} \) and \( D_{\nu^{\text{OC}}} \).

In some situations the finite magnitude of the reaction rates had to be
considered. From Equations (89) and (90) the ratio of the open-circuit voltage to the short-circuit current \( v_0/2 \) depends upon the flow rate through the sublayer thicknesses if the reaction rates are finite. Figure 13 shows a plot of \( \gamma_0 \) varying with sublayer thickness. This contradicts the common assumption that the reaction velocities are infinite and large enough to make the interfacial charge transfer limited by the charge transport from the fluid bulk \([4, 28]\).

A representative listing of the estimated parameters is given in Table 4. The first set of data with stainless steel cylinders shows that the \( k_1 = \rho_{1w} \) and the \( k_2 = k_1 \) tend to increase with temperature. The \( \rho_{1w} \) is also larger on the outer cylinder, consistent with the positive measured charge densities and negative \( \rho_{oc} \) and \( f_{sc} \) terminal measurements. The second set of data shows similar values for the \( \rho_{1w} \), at least for the lower temperatures. In that particular experiment, after reaching 70°C the voltage reversed polarity to become positive like the charge density, indicating that the \( \rho_{1w} \) on the outer cylinder became significantly larger than that on the inner cylinder. Subsequent measurements, given by the third set of stainless steel cylinder data, showed that this “conditioned” behavior of the system persisted; nominal reaction rates were also estimated, but the rates measured at 35°C were anomalously large. This analysis also showed that copper tends to have a slightly lower \( \rho_{1w} \) than the stainless steel. In contrast, EHV-Weidmann HiVal pressboard tended to have a slightly larger \( \rho_{1w} \) than the stainless steel. Quantitatively, these results are consistent with past estimates of \( \rho_{1w} \) \([7, 26, 28]\).

These measurements are also comparable to pipe flow measurements and analysis that have shown a \( \rho_{1w} \) of 5 mC/m³ and a reaction velocity of \( 3.8 \times 10^{-6} \) m/s for room temperature pressboard \([39]\).

Using these estimated values for the wall charge density and assuming an Arrhenius temperature dependence, the activation energy associated with the wall charge density could be calculated. More specifically, it was assumed that \( \rho_{1w} \) obeyed the relation

\[
\ln(\rho_{1w}) = c_1 - \frac{W_i}{kT}
\]  

where \( c_1 \) is a scaling coefficient, \( W_i \) is the activation energy, \( k \) is Boltzmann’s constant, and \( T \) is the temperature in Kelvin. A least-squares fit was then performed to determine the \( c_1 \) and \( W_i \) for both interfacial materials in each experiment. A summary of the estimated activation energy and analysis for each experiment is given in Table 4.
Table 4. Representative estimated values for the interfacial parameters using the Abedian-Sonin boundary condition. The outer cylinder was always bare stainless steel. Asterisked values indicate a poor fit in the estimation ($\chi^2 > 1$), as calculated from Equation (115). The first set of stainless steel values correspond to Figure 10 while the 'HiVal' values correspond to Figure 11. The data corresponding to the remaining values can be found in [11].

<table>
<thead>
<tr>
<th>Inner cylinder</th>
<th>T (°C)</th>
<th>$k_1$ (µm/s)</th>
<th>$\rho_1^w$ (mC/m³)</th>
<th>$k_2$ (µm/s)</th>
<th>$\rho_2^w$ (mC/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>stainless steel</td>
<td>15</td>
<td>1.53</td>
<td>3.23</td>
<td>2.83</td>
<td>2.23</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>2.22</td>
<td>9.29</td>
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<td>9.54*</td>
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<td>1.82</td>
<td>1.21</td>
<td>1.93</td>
<td>0.91</td>
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<td></td>
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<td>5.25</td>
<td>-</td>
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<td>-</td>
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<td>43.5</td>
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<td>HiVal (over copper)</td>
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<td>-</td>
<td>0.58</td>
<td>-</td>
</tr>
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<td></td>
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<td>0.77</td>
<td>-</td>
<td>1.46</td>
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<tr>
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<td>50</td>
<td>1.27</td>
<td>-</td>
<td>2.43</td>
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<td></td>
<td>70</td>
<td>2.18</td>
<td>-</td>
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<td>7.11</td>
<td>-</td>
<td>0.45*</td>
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<td></td>
<td>35</td>
<td>10.1</td>
<td>-</td>
<td>1.58</td>
<td>-</td>
</tr>
<tr>
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<td>15.0</td>
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<td>1.61</td>
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<td>0.03</td>
<td>0.02*</td>
<td>0.04</td>
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<td>10.2</td>
<td>-</td>
<td>3.58</td>
<td>-</td>
</tr>
<tr>
<td>HiVal (over copper)</td>
<td>15</td>
<td>3.56</td>
<td>-</td>
<td>0.13*</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>5.96</td>
<td>-</td>
<td>0.89</td>
<td>-</td>
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<td>7.71</td>
<td>2.84</td>
<td>1.84</td>
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<td>9.43</td>
<td>-</td>
<td>3.66</td>
<td>-</td>
</tr>
</tbody>
</table>

energies, given in Table 5, indicates that the copper (~0.28 eV) and the stainless steel (~0.25 eV) interfaces tend to have larger activation energies than the pressboard interface (~0.16 eV). The values for the $c_i$ are not listed because they had large variations between samples.

One set of data which highlights the difference between the Abedian-Sonin ($\rho^w$) boundary condition and the general boundary condition derived here is shown in Figure 14. For this particular set of data, the Abedian-Sonin condition underestimates the value of $P_2$ at low flow rates (large sublayer thicknesses), but overestimates the $P_2$ at high flow rates (small sublayers). Although the data points used in the estimations show considerable scatter, the trends are quite clear. The better fit by the general model cannot be attributed simply to the extra model parameter $K_2^S$ since the final fit for each temperature above 15°C only had one free parameter ($\xi_2 k_2^{\text{f}} / k_2^S$) in the estimation, which is equivalent to the fitting of a single parameter ($\rho_2^w$) in the Abedian-Sonin condition.

Another set of data that shows the difference between the boundary conditions is illustrated in Figure 15. The plots on the left side show the normalized data while the plots on the right side show the calculated parameters. This experiment had copper on the inner cylinder and

Table 5. Calculated activation energies for the estimated wall charge densities of Table 4 and Figure 16 assuming the Arrhenius temperature dependence of Equation (118). The additive concentration is listed for experiments which used BTA.

<table>
<thead>
<tr>
<th>Inner cylinder</th>
<th>$W_1$ (eV)</th>
<th>Outer cylinder</th>
<th>$W_2$ (eV)</th>
<th>[BTA] ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>stainless steel</td>
<td>0.29 ± 0.07</td>
<td>stainless steel</td>
<td>0.26 ± 0.01</td>
<td>-</td>
</tr>
<tr>
<td>steel</td>
<td>0.22 ± 0.01</td>
<td>steel</td>
<td>0.29 ± 0.04</td>
<td>-</td>
</tr>
<tr>
<td>copper</td>
<td>0.28 ± 0.01</td>
<td>stainless steel</td>
<td>0.31 ± 0.02</td>
<td>-</td>
</tr>
<tr>
<td>HiVal</td>
<td>0.15 ± 0.02</td>
<td>stainless steel</td>
<td>0.53 ± 0.26</td>
<td>-</td>
</tr>
<tr>
<td>HiVal (over copper)</td>
<td>0.16 ± 0.01</td>
<td>stainless steel</td>
<td>0.36 ± 0.02</td>
<td>-</td>
</tr>
<tr>
<td>HiVal (over copper)</td>
<td>0.19 ± 0.02</td>
<td>steel</td>
<td>0.32 ± 0.01</td>
<td>0</td>
</tr>
<tr>
<td>HiVal (over copper)</td>
<td>0.17 ± 0.03</td>
<td>steel</td>
<td>0.24 ± 0.05</td>
<td>3</td>
</tr>
<tr>
<td>HiVal (over copper)</td>
<td>0.17 ± 0.10</td>
<td>steel</td>
<td>0.25 ± 0.06</td>
<td>6</td>
</tr>
<tr>
<td>HiVal (over copper)</td>
<td>0.15 ± 0.08</td>
<td>steel</td>
<td>0.25 ± 0.38</td>
<td>4</td>
</tr>
<tr>
<td>HiVal (over copper)</td>
<td>0.14 ± 0.04</td>
<td>steel</td>
<td>0.24 ± 0.09</td>
<td>8</td>
</tr>
<tr>
<td>HiVal (over copper)</td>
<td>0.22 ± 0.01</td>
<td>steel</td>
<td>0.13 ± 0.07</td>
<td>19</td>
</tr>
<tr>
<td>HiVal (over copper)</td>
<td>0.24 ± 0.06</td>
<td>steel</td>
<td>0.21 ± 0.07</td>
<td>33</td>
</tr>
<tr>
<td>HiVal (over copper)</td>
<td>0.23 ± 0.03</td>
<td>steel</td>
<td>0.23 ± 0.05</td>
<td>52</td>
</tr>
<tr>
<td>HiVal (over copper)</td>
<td>0.24 ± 0.02</td>
<td>steel</td>
<td>0.26 ± 0.06</td>
<td>53</td>
</tr>
</tbody>
</table>

Figure 14. A comparison of the model fits to $P_2$ at four temperatures for the 53 ppm BTA electrification data of Figure 2.43 of [11]. The solid lines correspond to the general condition (Equation (100)) with $k_2^S$ nonzero while the dashed lines correspond to the Abedian-Sonin $\rho^w$ boundary condition (Equation (104)). The estimated parameters for the general condition are listed in Table 7.
stainless steel on the outer cylinder. By repeatedly switching the measurement mode of the electrometer connected between the cylinders, the open-circuit voltage, short-circuit current and core charge density were accurately measured at each flow rate. The value of $D_p\rho_p$ was then calculated from these measurements using Equation (92). The error bars on the data indicate a small variation in the measurements. The other method for obtaining $D_p\rho_p$ by measuring $\rho_p$ for several applied voltages and calculating the slope, was noisy and had larger variations because it was more sensitive to slight drifts in the system parameters (e.g. temperature and material conductivity) which led to charge density fluctuations that were comparable to the measured $D_p\rho_p$. As predicted from Equation (91), there is a slight variation in the charge density with the terminal constraint, decreasing slightly as the terminals are short-circuited. The dashed lines in Figure 15 show the fit of the Abedian-Sonin boundary condition model ($K_e \gg 1$ limit) to the data. The value of $P_3$ is set to zero because this boundary condition cannot have a negative value for $P_3$. The solid lines show the fit of the data to the general boundary condition of Equations (99) to (102). The $K_e \ll 1$ limit gave the smallest least-squares error in each case. It still did not fit the parameter $P_3$ well, but it does allow for negative values in $P_3$. To improve the fit to $P_3$, it may be necessary to model the dynamics of the individual charge species, rather than the net charge and current densities.

The estimated parameters corresponding to the lines in Figure 15 are listed in Table 6. While the wall charge densities in the Abedian-Sonin case are relatively large, the reaction velocity for the stainless steel/oil interface is comparable to the previous measurements. For the general condition, since the $K_e \gg 1$ limit gave the best fit, $\xi$ and $k_f^r$ could not be estimated individually. Estimates for $k_f^r$ of $1.54 \text{ s}^{-1}$ for copper and $0.473 \text{ s}^{-1}$ for the stainless steel were obtained. This value for the copper is suspect because it came from the fit to the parameter $P_3$ which was poor. To estimate the forward reaction rates, the $\xi$ can be set equal to the wall charge densities estimated from the Abedian-Sonin model (Equation (51)) with $\xi \approx \rho_{w}$ and $k_f^r = 0$. This gives a rough estimate of the forward reaction rates as $46.1 \text{ ppm/s}$ for copper and $11.4 \text{ ppm/s}$ for stainless steel. This stainless steel value is comparable to the $24.3 \text{ ppm/s}$ estimated from the Abedian-Sonin condition alone.

**Table 6.** Estimation results for the 70°C data in Figure 15. Note that $k_e$ in the Abedian-Sonin condition (Equation(26)) corresponds to $k_f^r$ in the general boundary condition (Equation (66)).

<table>
<thead>
<tr>
<th>Material</th>
<th>Abedian-Sonin $\rho_{w} \text{ mC/m}^2$</th>
<th>General Condition $k_f^r \text{ mC/m}^2$</th>
<th>$\xi k_f^r / k_f^s \text{ C/m}^2$</th>
<th>$k_f^r \text{ s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>copper</td>
<td>9.78</td>
<td>29.3</td>
<td>10.85</td>
<td>1.54</td>
</tr>
<tr>
<td>stainless steel</td>
<td>20.5</td>
<td>49.6</td>
<td>10.08</td>
<td>0.473</td>
</tr>
</tbody>
</table>

Figure 15. A comparison of the model fits to the normalized electrification data from Figure 12 of [10] for a copper sleeve on the inner cylinder and a stainless steel outer cylinder. The solid lines correspond to the general condition (Equations (99) to (102)) while the dashed lines correspond to the Abedian-Sonin boundary condition (Equations (103) to (106)). The estimated parameters are listed in Table 6.

5.3. EFFECTS OF BTA

Parameter estimations were also performed on electrification data taken as the antistatic additive BTA was added to the oil (see Figure 21 of...
For the initial comparison, the Abedian-Sonin boundary condition was fit to the data. Good estimates of the volume charge densities on the liquid side of the interfaces were obtained, but the uncertainty in the pressboard conductivity prevented an accurate determination of the reaction rates. Figure 16 shows the estimated $\rho_w^v$ as the BTA concentration was varied. In general, the BTA reduced the $\rho_w^v$ for both the pressboard/oil and the stainless steel/oil interfaces with approximately 7 ppm BTA being a critical concentration for the reduction. Increasing the concentration beyond this yielded slight further reductions in $\rho_w^v$. From Table 5, the BTA did not appear to affect the activation energy of the wall charge densities significantly.

Assuming the viscosity is independent of the BTA concentration, then the ion mobility can be reduced if the average radius of the ion increases. Thus, if the BTA forms molecular complexes or becomes attached to the charge carriers, the average size of the ion increases and the mobility decreases. In terms of the measured conductivity ($\sigma_2 = q\varepsilon\pi_n(b_+ + b_-)$), the net mobility ($b = b_+ + b_-$) can be expressed as

$$b_{(\text{with BTA})} = b_{(\text{no BTA})} \frac{\sigma_2' (\text{with BTA})}{\sigma_2 (\text{no BTA})}$$

(120)

From Equation (5) the molecular diffusivity is also affected by the BTA so that the reduced mobility does not affect the normalizations of Tables 1 and 2 for the Debye length, the open-circuit voltage, or the short-circuit current. In contrast, the reduced mobility leads to a reduced magnitude for the normalized volume charge density. This has the effect of increasing the sensitivity of the $\rho_w^v$ estimation to the terminal voltage. When applied to the electrification data, the $\rho_w^v$ still tends to decrease as the BTA concentration increases, as shown in Figure 17, but the decrease is not as dramatic as that shown in Figure 16.

This shows that both conductivity reduction mechanisms for the BTA leads to a reduction in $\rho_w^v$. While Figure 17 also shows the $\rho_w^v$ reversing polarity as the BTA concentration increases, the numerical fit to the data was relatively poor. This, coupled with the observation that the wall charge densities do not always monotonically increase with temperature, suggests that the simple model for a BTA dependent mobility is probably not reasonable. Undoubtedly, the BTA affects both the number density of the ions and the ion mobility.

To explore a possible mechanism for the BTA affecting both the number density of the ions and the ion mobilities, the Langevin model for recombination can be used. Under equilibrium conditions, the rate of generation of ions ($G$) balances the recombination rate ($R$) as

$$G = R = \alpha \rho_c^2 = \left(\frac{b_+ + b_-}{\varepsilon_2}\right) \rho_c^2$$

(121)

with $\alpha = (b_+ + b_-)/\varepsilon_2$ the Langevin recombination coefficient and $\rho_c = q\varepsilon\pi_n$ the charge density of dissociated positive and negative charge carriers. The charge generation rate ($G$) will be approximately constant at a given temperature if the neutral species only weakly dissociate into ions so that the number density of the neutrals is essentially constant. Combining the oil conductivity ($\sigma_2 = \rho_c(b_+ + b_-)$) and Equation (121), the average charge density of the carriers and the conductivity can be solved as

$$\rho_c = \sqrt{\frac{\varepsilon_2 G}{b_+ + b_-}}$$

(122)

$$\sigma_2 = \sqrt{\varepsilon_2 G (b_+ + b_-)}$$

These equations indicate that if the mobility decreases, the conductivity also decreases even though the density of ions actually increases. Similar to the previous limiting case, the net mobility can be expressed in terms of the measured conductivities as

$$b_{(\text{with BTA})} = b_{(\text{no BTA})} \left(\frac{\sigma_2' (\text{with BTA})}{\sigma_2 (\text{no BTA})}\right)^2$$

(123)

When incorporated into the parameter estimation routine, results similar to Figure 17 are obtained.

Although the Langevin model is plausible, the best results in the parameter estimation routine were obtained when only the ion number...
density was dependent upon the BTA concentration. This can be obtained from the Langevin model if it is assumed that the generation rate $G$ is affected by the BTA so that the number density of the ions varies with $\sqrt{G}$ while the mobility is held constant. Then, at low BTA concentrations the generation rate is assumed to increase with the number of neutrals available for dissociation then the ion number density and the oil conductivity should decrease. Evidence for this conductivity variation with BTA concentration was observed in the experiments, as in Figure 20 of [10]. Admittedly, there are numerous assumptions incorporated into this model, but this provides a possible mechanism for the role of BTA.

Although the model incorporating the Abedian-Sonin boundary condition usually gave the best fit to the data, the data taken with BTA was an exception. The Abedian-Sonin condition (limiting case 1) almost always gave the best fit to the open-circuit data for the inner cylinder (the pressboard/oil) interface but usually did not give the best fit to the data for the outer cylinder (the stainless steel/oil) interface. A summary of the estimation results for the outer cylinder interface are given in Table 7. The most consistent results appeared at 35°C in which the estimation showed a gradual transition from $K_2^o = 1$ to $K_2^o << 1$ with the addition of BTA. Since the value of $k_2^o/k_2^o$ did not appear to change appreciably, it appears that this transition was caused by the decreasing oil conductivity. Reasonable results were not obtained for the estimation on the parameters $P_2$ and $P_4$ for two reasons. First, the uncertainty in the pressboard conductivity was large and if the $K_2^o$ are small then uncertainties in $\sigma_1$ or $\sigma_4$ can lead to negative values for the $K_2^o$, which are not physically reasonable. Second, the measurements of $D_o\rho_o$ were noisy, which again can lead to non-physical (negative) values for the $K_2^o$.

### 6. SUMMARY

One of the least understood processes in flow electrification of semi-insulating materials is the interfacial charge transfer boundary condition. In an attempt at improving this understanding, this paper developed a chemical reaction-based boundary condition which reduces to the commonly used Abedian-Sonin 'wall' charge density condition as a limiting case. The chemical reaction based boundary condition provides a physical description of the wall charge density in terms of the difference in adsorption and desorption rates for the individual ionic species and also predicts heterocharge and homocharge configurations in the presence of an applied electric field. When incorporated into a self-consistent model for the flow electrification between rotating cylinders, expressions similar in form to those obtained from the Gavis-Koszma charge density gradient condition were found as a limiting case. This was somewhat surprising since the assumptions for the boundary conditions were different and the model also indicated that the Gavis-Koszma condition was flawed, at least when applied to systems containing two solid/liquid interfaces as opposed to the commonly treated pipe flow models.

The electrification model between rotating cylinders was also compared to several sets of experimental data. The Abedian-Sonin boundary condition was able to describe measurements covering a wide range of operating conditions. Under open-circuit conditions, without current flowing across the interfaces, estimates of the volume charge densities on the liquid side of the interfaces provide good fits between the model and the measured data. Under short-circuit and applied voltage conditions, when current flows across the interfaces, the fits were poor but the measured data indicates that the interfacial charge transfer reaction rates were not 'infinite' and the interfacial chemical reactions could not maintain the equilibrium charge density. Low concentrations (< 10 ppm) of BTA reduced the wall charge density but did not appreciably affect the reaction rate constants. Since the boundary condition developed here is an extension of the wall charge density condition, a wider range of data could be qualitatively and quantitatively described. While the measurement uncertainty and noise prevented estimations of all of the interfacial parameters and rate constants, the chemical reaction based boundary condition provides additional insight into the interfacial charge transfer processes.

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