

A Theoretical and Numerical Study on Electrification and Flow inside Electrostatic Atomizers

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THESIS

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This thesis is dedicated to Sosan and Nafis.

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Contribution of Authors

Chapter 2 provides an overview of the theoretical and numerical models developed to study the electrification, near-electrode layers and internal electrohydrodynamic flow in electrostatic atomizers.

Chapter 3 represents two published papers (1. Kashir, B., Perri, A. E., Yarin, A. L., Mashayek, F. Numerical investigation of ionic conductor liquid charging at low to high voltages. *Phys. Fluids* **2019**, 31, 021201 and Kashir, B., Perri, A. E., Yarin, A. L., Mashayek, F. 2. Electrification mechanism and constituted near-electrode layer inside electrostatic atomizers. 29th Conference on Liquid Atomization and Spray Systems, Paris, France 2019) in which I am the first author. Dr. Farzad Mashayek supervised the research and assisted with reviewing the manuscript. Dr. Alexander Yarin led the experimental group and assisted with reviewing the manuscript. Anthony Perri assisted with reviewing the manuscript. I implemented the numerical model in OpenFOAM platform, performed the numerical simulations, postprocessing and analyzing the results, and writing the manuscripts.

Chapter 4 represents one published paper (Kashir, B., Perri, A. E., Mashayek, F., Yarin, A. L. Theoretical and numerical study of formation of near-electrode layers in ionic conductor liquids at high voltages. *Langmuir* **2019**, 35, 11080-11088) in which I am the first author. Dr. Farzad Mashayek supervised the research and assisted with reviewing the manuscript. Dr. Alexander Yarin developed the theory of non-specific adsorption and assisted with reviewing the manuscript. I performed the numerical simulations, postprocessing and analyzing the results, and writing the manuscript. Anthony Perri assisted with reviewing the manuscript.

Chapter 5 represents one published paper (Kashir, B., Perri, A. E., Yarin, A.L., Mashayek, F. Slow discharge theory and calculation of the potential drop across the compact layer at high electrode voltages. *Langmuir* **2019**, 35, 14458-14464) in which I am the first author. Dr. Farzad Mashayek supervised the research and assisted with reviewing the manuscript. Dr. Alexander Yarin assisted with reviewing the manuscript. I employed the theory to provide required formulations, performed numerical simulations, postprocessing and analyzing the results, and writing the manuscript. Anthony Perri assisted with reviewing the manuscript.

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NOMENCLATURE

Roman Symbols

a_0	Radius of the sphere of ions	m
A	Hamaker constant	J
A_0	Single-ion-occupied site	m^2
c_{*i}	Ion concentration	$\frac{1}{m^3}$
$c_{*\infty}$	Bulk concentration	$\frac{1}{m^3}$
$\bar{c}_i$	Cross-sectional average of ions	
C_1	Coefficient of the attractive part	Jm^6
C_2	Coefficient of the repulsive part	Jm^{12}
d	Characteristic diameter of interacting bodies	m
D	Diffusivity coefficient	$\frac{1}{m^2s}$
$\mathbf{E}_*$	Electric field vector	$\frac{V}{m}$
$\mathbf{E}_{*ext}$	Externally applied electric field vector	$\frac{V}{m}$
$\mathbf{E}_{*\tau}$	Tangential electric field	$\frac{V}{m}$
F	Faraday constant	$\frac{As}{mol}$
F_C	Coulombic force	N
F_W	van der Waals force	N
e	Elementary charge	C
ΔG_*	Electron transfer activation energy	$\frac{J}{mol}$
H_*	Channel height	m
h_*	Half-channel height	m
J_{e*}	Electric current density	$\frac{A}{m^2}$
j_{*i}	Ion flux	$\frac{1}{m^2s}$

j_{0*}	Exchange current density	$\frac{A}{m^2}$
j_{*spray}	Spray current	$\frac{A}{m}$
K	Dimensionless parameter	
K_1	Integration constant	
K_2	Integration constant	
K_3	Integration constant	
K_4	Integration constant	
$k_{b,i}$	Kinetic coefficient of desorption at the i-th layer	
$k_{f,i}$	Kinetic coefficient of adsorption at the i-th layer	
k_B	Boltzmann constant	$\frac{m^2 kg}{s^2 K}$
L	Dimensionless length	
ℓ	Distance from bulk to the electrode	m
n_i	Grid points in i direction	
n_{tot}	Total number of grid points	
$n_{eq}^{\pm}$	Equilibrium number of ions present in the unit surface area of compact layer	
p_*	Pressure	$\frac{kg}{ms^2}$
q_*	Charge density	$\frac{C}{m^3}$
r_*	Distance between interacting ingredients	m
R_O	Twice the distance from the center of electron-transfer participating ions toward	
electrode		m
Re	Reynolds number	
T	Temperature	K
u_*	Axial component of velocity	$\frac{m}{s}$
u_{*in}	Maximum inflow velocity in axial direction	$\frac{m}{s}$
u_{*Sm}	Smoluchowski-driven velocity	
V_{0*}	Electrode potential	V
$\mathbf{V}_*$	Velocity vector	m

W	Lennard-Jones Potential	J
X	Stretched coordinate	
x_*	Coordinate	m
Δx_*	Cell size in x_* direction	m
y_*	Coordinate	m
Δy_*	Cell size in y_* direction	m
z_{OX}	Valence of products in an oxidation reaction	

Greek Symbols

α	Dimensionless parameter	
β	Dimensionless parameter	
ϵ	Solvent dielectric permittivity	
ϵ_0	Vacuum permittivity	$\frac{F}{m}$
ϵ_{op}	Optical dielectric constant	
ϵ_S	Static dielectric constant	
ϵ_1	Dimensionless parameter	
η_*	Over-potential	V
ζ	Zeta potential	V
λ_D	Debye screening length	m
λ_S	Compact layer thickness	m
λ_d	Polarized diffuse layer thickness	m
λ_{el}	Reorganization energy	J
μ	Dynamic viscosity	$\frac{kg}{ms}$
ρ_*	Density	$\frac{kg}{m^3}$
ρ_i	Volumetric number density at the i-th layer	$\frac{1}{m^3}$
σ	Electric conductivity	$\frac{S}{m}$
σ_i	Ion density per unit area at i-th layer	$\frac{1}{m^2}$
$\theta_i^\pm$	Parts of non-conducting islands with i layers of ions atop	
τ_c	Charge relaxation time	s

τ_H	Hydrodynamic time scale	s
φ_*	Electric potential	V
ψ_1	Electric potential at the interface of compact and diffuse layers	V

Other Symbols

$*$	Dimensional variable	
∇	Gradient operator	$\frac{1}{m}$
∇^2	Laplacian operator	$\frac{1}{m^2}$

SUMMARY

Electrostatic atomization has appeared as a desired technology in distinct industrial applications such as painting, coating, and injection in diesel engines. It yields controlled spray trajectories, enhanced dispersion/deposition efficiency, and increased evaporation compared to traditional atomization methods. Furthermore, it prohibits common coating problems such as uneven or over-application of oil. It demands less energy and provides applicability to a wide range of fluid viscosity.

The so-called leaky dielectric liquids are the best candidates for electrostatic atomizers due to their enhanced charge residence time compared to conducting liquids such as water, where the charges would instantly relax to the surface. The leaky dielectric liquid concept emerged in the mid-'60s to explain electrohydrodynamic phenomena in liquids previously considered as insulators, such as vegetable oils. These ionic conductor liquids are capable of possessing a small net charge resulting in a relatively low conductivity. The origin of ions in such liquids is still under debate. In electrostatic atomizers, electrodes are perfect conductors capable of passing through an electric current and sustaining faradaic reactions. However, in non-conducting surfaces, only embedded charges remain and there is no sustained electric current at the surface.

In this study, the electrification and ion transport in ionic conductor liquids (oils) are studied theoretically and numerically while allowing for the Frumkin-Butler-Volmer kinetics responsible for the electron transfer at the metal electrodes. The numerical model solves the fluid flow equations along with the electrostatic equations. The fluid flow equations are the continuity and momentum equations. The source term in the momentum equation accounts for the Coulombic body force responsible for the electro-osmotic flow. The electrostatic equations are the anion and

cation transport equations, along with the Poisson equation. As a sample case, a channel flow is considered with the charging electrodes to occupy the middle part of the channel while other sections are electrically insulated. The considered ionic conductor liquid throughout this study is canola oil.

The constituted near-electrode layers across the electrode in the outwards direction are compact and diffuse layers, respectively. The ions present in the compact layer do not participate in the electrohydrodynamic flow. Hence, the computational model at the electrode surface starts from the interface of the compact and diffuse layers. In ionic conductor liquids with very low permittivity, such as canola oil, 99% of the potential drop occurs across the compact layer. This drop makes finding the electric potential value at the interface of compact and diffuse layers crucial since it is used as a boundary condition for the provided computational model. On the other hand, most of the potential drop in aqueous solutions occurs in the diffuse layer, which is not the case in this study.

The electric potential boundary condition at the electrode surface of the considered channel flow case is a fixed value (Dirichlet-type boundary) with orders of magnitude lower than the applied voltage at the electrode surface. The ionic boundary conditions at the electrode surface are Neumann-type conditions. Further comprehension of the characteristics of the compact Stern and diffuse layers in electrostatic atomizers enables us to apply a more accurate electric potential boundary condition for the electrode surface in the provided numerical model.

A novel theoretical approach is developed to correlate the thickness of the equivalent one-dimensional compact layer to the potential drop across this layer. These electrodes are subjected to high voltage and sustain an electric current. The non-specific (non-electric) ion adsorption responsible for creating the compact Stern layer is attributed to the Langmuir-Brunauer-Emmet-

Teller mechanism. Faradaic reactions are responsible for electron transfer at the open parts of the metallic electrode surface. In contrast, the compact Stern layer is formed on the oxide or impurities at the electrode surface.

The electron transfer regime in electrostatic atomizers with electrodes exposed to high voltages is kinetic-limited. Hence, we employ the Frumkin slow discharge theory combined with the Marcus electron transfer theory to present another novel approach to predict the electric potential at the interface of the compact and diffuse layers. The activation energy of the electron transfer in the faradaic reaction is found from the Marcus theory. The ionic concentration and net charge distribution across the polarized diffuse layer are calculated from the numerical simulations given the known counter-ion flux value at the electrode surface from the concurrent experimental measurements. With the concentration of ions at the interface of compact and diffuse layers be known and employing Frumkin slow discharge theory, the electric potential value at the interface is found from a predictor-corrector algorithm that is detailed with examples.

The provided numerical and theoretical models thoroughly demonstrate the electrification mechanism, constituted near-electrode layers and internal electrohydrodynamic flow in electrostatic atomizers. We found in the channel flow case that the role of Smoluchowski slip near the electrodes is negligibly small compared to the viscous scraping of the polarized layer under any realistic values of the imposed longitudinal electric field. This means that ions are removed from the polarized diffuse layer by the visocus scraping mechanism in electrohydrodynamic flow inside electrostatic atomziers, rather than the Coulombic force.

1. INTRODUCTION

1.1. Motivation and objectives

Electrostatic atomization has appeared as a promising technology in many industrial applications such as the oil coating, painting, and fuel injection in combustion chambers of diesel engines¹⁻². It provides controlled spray trajectories, enhanced dispersion efficiency, and efficient evaporation while avoiding uneven or over-application of oil than conventional atomization approaches³⁻⁴.

Despite the desirable features of this technology, the electrification mechanism and the parameters affecting the resulting net charge at the outlet are unknown. These are vital parameters in designing industrial devices employing this technology. The motivation of the current study is to provide a fundamental background to explain the charging phenomenon and internal electrohydrodynamic flow in electrostatic atomizers. Unfortunately, the constituted near-electrode layers in these high-voltage electric current-carrying electrodes are not well understood. Due to substantial differences with the low voltage (less than 3 volts) regime, the available electrochemical theories in this regime do not apply to the electrostatic atomizers

The characterization of near-electrode layers would help demonstrate the internal electrohydrodynamic flow due to counter-ion discharge at the electrode surface. This discharge creates a polarized diffuse layer. Transport of ions present in the polarized diffuse layer occurs due to viscous scraping. Figure (1.1) illustrates an electrostatic atomizer schematic, the supply line, and the constituted near-electrode layers. As depicted, the computational model at the electrode surface starts from the interface of compact and diffuse layers. This makes the recognition of the properties of this interface imperative.

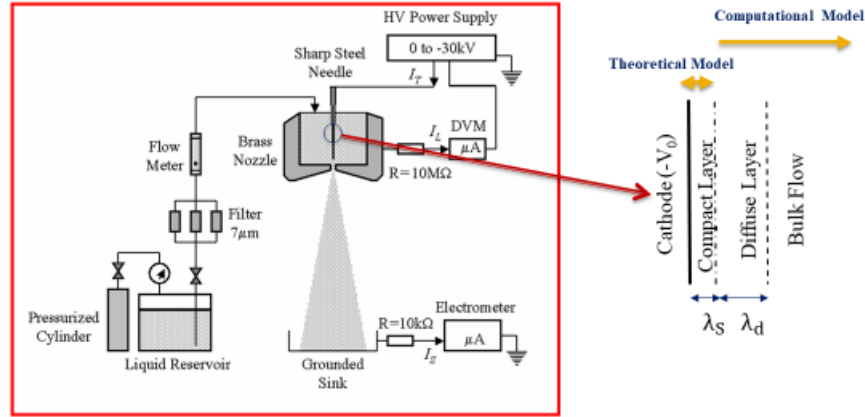


Figure 1.1. A schematic of the electrostatic atomizer and the supply line. The near-electrode layers and the starting surface of the computational domain at the electrode surface are indicated.

The first objective of this study is to provide a numerical model capable of demonstrating the internal electrohydrodynamic flow in electrostatic atomizers. The measured electric current at the electrode surface is a consequence of counter-ion discharge. The numerical model should accommodate the realistic electron transfer faradaic reactions based on the Butler-Volmer-Frumkin equation³⁵ and the measured electric current density values in experimental investigations. The electric potential boundary condition at the electrode surface is challenging for the computational model. Due to the low permittivity of canola oil, there is a substantial potential drop across the compact layer. The electric potential at the interface of compact and diffuse layers is significantly lower than the applied voltage at the electrode surface.

The second objective is to find the electric potential value at the interface of diffuse and compact layers by characterizing the constituted near-electrode layers. These layers, including the compact Stern layer and the polarized diffuse layer, are not previously studied for high voltages. Knowing their characteristics is imperative to apply accurate Dirichlet-type boundary conditions for electric potential at the interface of compact and diffuse layers.

1.2. Structure of the dissertation

The thesis investigates the fluid flow and charging mechanism inside the electrostatic atomizers. The second chapter discusses the fundamental and related literature regarding constituted near-electrode layers in conventional electrochemical systems. The concept of ionic conductor liquid and the current computational methods targeting internal electrohydrodynamic flow are explained. Furthermore, the differences between conditions in electrostatic atomizers with the ion-exchange membranes are illustrated.

Chapter 3 explains the numerical methodology and the governing equations solved within the computational model. The sample case of internal electrohydrodynamic flow inside a microchannel with the middle section composed of electric current-carrying electrodes is solved. The resulting spray current and the transport of ions are demonstrated.

Chapter 4 describes the proposed theoretical models to characterize the constituted near-electrode layers in electrostatic atomizers. The thickness of the compact Stern layer is calculated by employing the developed theoretical model based on the Langmuir-Brunauer-Emmet-Teller adsorption mechanism⁶¹.

Chapter 5 illustrates the employment of Frumkin slow discharge theory⁴⁷ to find the electric potential at the interface of compact and diffuse layers. The activation energy of the electron transfer reaction is calculated through the Marcus electron transfer theory⁴⁹.

2. LITERATURE REVIEW

2.1. Introduction

This section is divided into three parts. First, we review the concept of the leaky dielectric model and the available computational models for ionic conductor liquids in the context of an electrohydrodynamic flow, such as the charge injection method. Also, we demonstrate the differences between our case and the ion-exchange (permselective) membranes.

In the second part, we review the available models for the Stern compact layer. The deficiencies in these models, which makes them inapplicable to the case of high-voltage electrification in electrostatic atomizers, are demonstrated. Also, we elaborate on the constituted near-electrode layers in electrostatic atomizers and their characteristics.

In the last part, we demonstrate the characteristics of the heterogeneous electron transfer in faradaic reactions occurring at the electrode surface. These characteristics enable the deployment of Frumkin slow charge and Marcus electron transfer theories to calculate the electric potential at the interface of compact Stern and diffuse layer in the context of electrostatic atomizers.

2.2. Leaky dielectric model and the previous computational research

The leaky dielectric model was first suggested in the 60s to demonstrate the charging characteristics of previously known insulating liquids⁵⁻⁷. Liquids such as refrigerants and transformer oils were earlier known as dielectric liquids⁸⁻⁹. Later, it was revealed that these liquids possess a very low electric conductivity, which is responsible for electrohydrodynamic effects. They express the properties of weak electrolytes⁷⁻⁸ and can feature near-electrode polarized layers. For non-conducting surfaces sustaining no electric current and possessing embedded charges, the thickness of the polarized layer is on the order of the Debye length¹⁰⁻¹¹. Imposing a tangential electric field to the non-conducting electrode would lead to Smoluchowski-driven flow due to the

Coulombic force acting on the charges in the polarized layer¹²⁻¹³. Electrodes in electrostatic atomizers are perfect metallic conductors sustaining an electric current due to the faradaic reactions¹⁴⁻¹⁷ occurring at the electrode surface.

The computational study on the internal electrohydrodynamic flow of poorly conducting liquids in electrostatic atomizers is mainly performed based on the charge injection theory¹⁸⁻²⁰. The well-known blade-plane geometry¹⁸⁻²⁰ is studied vastly through unipolar ion injection at the metallic electrode/electrolyte²¹ interface. In electrostatic atomizers, electrodes are exposed to high voltages in the range of kV. The charge injection theory ignores the transport of ions (charges) across the electrode surface due to faradaic reactions. It considers a fixed, known value as the charge density boundary condition at the metal/liquid interface. Subsequently, the charge transport equation is solved across the domain along with the fluid flow equations to determine the volumetric charge density and the Coulombic body force in electrohydrodynamic flow. The electrohydrodynamic plumes created by a sharp blade electrode in contact with an ionic conductor liquid is investigated thoroughly with charge injection theory employing different injection laws²². An unsteady regime is predicted depending on parameters such as electric mobility, blade shape, and injection strength²². Charge injection theory is combined with the lattice Boltzmann method to study the three-dimensional electroconvection of dielectric liquids²³. It should be emphasized that in charge injection theory, there is no physical relationship between the applied voltage and the sustained electric current at the electrode surface. Moreover, the boundary condition for the charge density at the electrode surface is of the Dirichlet type with assumed values.

On the other hand, the charge density value at the electrode surface can be found by solving the ionic transport equations with appropriate boundary conditions considering the measured electric current at the electrode/electrolyte interface²⁴⁻²⁵. These studies account for the constituted

compact Stern layer at the electrode surface and electron transfer through faradaic reactions. For instance, a combined mathematical and computational method is developed to model the classical diffusion-limited regime of the electrochemical thin film under DC current²⁶. Non-linear boundary conditions related to the reaction kinetics and the compact layer capacitance are also taken into account²⁷. The simplified set of equations appropriate for low-voltage applications (less than 3 V) is employed²⁸ compared to more generic cases dealing with high voltage electrification in ionic conductor liquids.

In electrostatic atomizers, we deal with the case of oil charging in contact with metallic electrodes sustaining an electric current. Our proposed computational method accounts for the ions transport in electrohydrodynamic flow coupled with the kinetics of faradaic reactions at the electrode surface. It is applicable at all voltages (low to high). The previous proposed solvers²⁹ and approaches²⁶⁻²⁷ were either tailored for low voltage operating conditions through a simplified set of transport equations or not considering the electron transfer at the electrode/electrolyte surface. The present work employs the electrohydrodynamic flow governing equations in general form with no simplifications (valid for all cases) with or without ion flux at the electrode surface to provide a comprehensive numerical model.

It is important to note that here we target a completely different situation than the ion-exchange membranes³⁰⁻³⁴. Such membranes possess an embedded charge density and merely allow crossing counter-ions as a consequence of concurrent diffusion and electric mobility. Counter-ion discharge and ionization due to faradaic reactions are neglected in such cases. Hence, the Frumkin-Butler-Volmer equation does not apply to these cases³⁵⁻³⁶. In permselective membranes, an imposed constant concentration of counter-ions at the surface acts as a counterbalance to the fixed charge concentration inside the membrane. Due to the developing hydrodynamic instability in the near-

surface layer, these membranes operate even above the diffusion-limited regime³⁷ (far from the kinetic-limited regime in our case). The flow in ion-exchange membranes is merely electric-driven. Although, in some cases, such as the electrodialysis stacks, a non-electrically driven forced flow might exist.

On the other hand, in electrostatic atomizers, faradaic reactions are sustained¹⁵⁻¹⁷ through the discharge of counter-ions or ionization of neutral ions. These electron transfer reactions are governed by the well-known Frumkin-Butler-Volmer. The recent experiments have indicated the kinetic-limited regime of electrification in these electrodes¹⁶⁻¹⁷. These slow faradaic reactions are called “glowing” similar to what is done for the corrosion reactions³⁸.

The current work aims to demonstrate the electrification and electrohydrodynamic flow in a model electrostatic atomizer with a flux of counter-ions compatible with concurrent experimental measurements¹⁶⁻¹⁷. An analytical solution for the near-electrode polarized layer is provided and used as a benchmark case to validate the numerical model. A two-dimensional problem associated with the bulk Coulomb force near a non-conducting polarized electrode is solved and compared with the available analytical solution¹²⁻¹³.

2.3. Stern compact layer and the presence of Butler-Volmer-Frumkin equation

The early and pioneering works of Butler, Volmer, and Frumkin demonstrated the kinetics of faradaic reactions occurring at the conducting electrode surface. The constituted layers near the conducting electrodes are the compact and diffuse layers^{35,36,39,40}. The applied electric potential at the electrode surface specifies the structure of these polarized layers. Following an applied high electric potential at the electrode surface, counter-ion crowding occurs in aquatic solutions, contributing to the thickness of the compact layer⁴⁰. However, in the case of oils in focus here, this ion crowding is barely feasible⁴¹. In liquids with low conductivity (such as the vegetable oils), the

near-electrode compact layer can only be created through the non-specific (non-electric) adsorption of ions described in the preliminary work of Stern⁴².

Stern considers the compact layer as a one-dimensional capacitor with constant capacity C_s . Stern assumed that the electrodes possess a ζ -potential that causes the polarization. Models, such as the Grahame⁴³, distinguish between the direct adsorption of ions or with the shell formed by polar molecules in aquatic solutions. It is interesting to note that such hydration is irrelevant in the case of oils. The Stern's or Grahame's models did not imply the electric current-carrying electrodes and faradaic reactions at the electrode surface. The effective thickness of the Stern compact layer is introduced in the work of Bazant et al^{27,28,40}. They used it as a free parameter to find the potential drop across the compact layer.

It is important to emphasize that the concept of a compact layer adjacent to an electrode goes back to the early works of Helmholtz⁴⁴ and Smoluchowski⁴⁵. In these early works and the subsequent ones, there was no electron transfer through the compact layer⁴⁶. The potential drop across the compact layer has a fundamental role in characterizing the constituted near-electrode layers. In previous works, the compact and diffuse layers were lumped together in the same domain, and the Stern electric potential boundary condition was applied for the entire domain^{42,27}. The physical reasons behind potential drop across the compact and diffuse layers differ^{36,42}. Not taking into account these different characteristics leads to predicting the electric potential at the interface of compact and diffuse layers less than 1 V regardless of the ionic flux value at the surface of the electrode⁴⁰. In cases with the applied voltage at the electrode in the range of kV¹⁶⁻¹⁷, imperfect demonstration of the characteristics related to the constituted near-electrode layers becomes problematic and results in faulty simulations. Hence, a detailed description of the

compact layer in high voltage electrode (the case electrostatic atomizer) is required and aimed in the current work

2.4. Slow discharge theory and Marcus electron transfer energy equation

The kinetics of the heterogeneous charge transfer reactions are demonstrated by the Frumkin slow discharge theory, which accounts for the electrostatic interaction of reactants and products across a charged interface⁴⁷. The Frumkin slow discharge theory can be rearranged based on the quantum-chemical approach of the Marcus theory⁴⁸. The Marcus electron transfer theory calculates the reaction rates of heterogeneous electrode reactions⁴⁹. The primary aspect of the Marcus theory is the quadratic dependence between the free energy (associated with the reactant and product) and the configurational reaction coordinate. This coordinate is at the intersection of potential energy parabolas, where the isoenergetic electron transfer happens. In this study, we utilize the Frumkin slow discharge theory to ascertain the electric potential value at the compact and diffuse layers interface. The activation energy of the electron transfer reaction is calculated from the Marcus electron transfer theory.

3. Numerical Investigation of Ionic Conductor Liquid Charging

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This chapter focuses on providing a numerical model for internal electrohydrodynamic flow. An analytical solution for the polarized boundary layer adjacent to a conducting electrode with faradaic reactions is provided, and the numerical model is validated against the analytical distributions. The distribution of ions and the ionic transport equation terms in a configuration similar to the realistic atomizers are demonstrated to provide a better comprehension of transport mechanisms in the after-electrode section and before ejecting the spray current from the atomizer orifice.

3.1. The polarized boundary layer of a conducting metallic electrode

Consider a conducting electrode with sustained electric current due to the faradaic reactions. Here, we assume the conducting electrode is a cathode with an applied electric potential of $-V_{0*}$ (with $V_{0*} > 0$). The flux of cations discharging at the cathode based on the Nernst-Planck equation yields:

$$j_*^+ = -D \frac{dc_*^+}{dx_*} - \frac{De}{k_B T} c_*^+ \frac{d\phi_*}{dx_*} = j_* \quad (3.1)$$

Here, j_*^+ is the cation flux; c_*^+ is the cation concentration with the units $1/\text{m}^3$; e is the elementary charge; D marks the diffusion coefficient; φ_* indicates the electric potential; T is the temperature and k_B represents the Boltzmann constant. x_* is the normal coordinate orienting toward the electrode. The electrolyte is considered to be 1:1. The asterisks identify the dimensional parameters.

The anion flux j_*^- is given by the following formulation accounting for the fact that anions do not participate in electron transfer at the cathode surface.

$$j_*^- = -D \frac{dc_*^-}{dx_*} + \frac{De}{k_B T} c_*^- \frac{d\varphi_*}{dx_*} = 0 \quad (3.2)$$

Here, c_*^- is the anion concentration with the units $1/\text{m}^3$. For simplicity, the diffusion coefficient for both anions and cations are considered to be identical ($10^{-11} \text{ m}^2/\text{s}$).

The Gauss law takes the form of a one-dimensional Poisson equation as:

$$\frac{d^2\varphi_*}{dx_*^2} = -\frac{e}{\varepsilon\varepsilon_0} (c_*^+ - c_*^-) \quad (3.3)$$

where ε_0 is the vacuum permittivity, and ε is the dielectric permittivity of the solvent.

The cathode is located at the $x_* = l$ from the electroneutral bulk domain. The boundary conditions at the electroneutral bulk imply:

$$x_* = 0, c_*^- = c_*^+ = c_{*\infty}, \varphi_* = 0 \quad (3.4)$$

with $c_{*\infty}$ being the bulk concentration of the electrolyte.

Equations (3.1)-(3.3) are rendered dimensionless with the following scales: l for x_* , $c_{*\infty}$ for c_*^- and c_*^+ , $k_B T/e$ for φ_* and V_{0*} and $Dc_{*\infty}/l$ for j_*^+ , j_*^- and j_* . The dimensionless equations take the following form:

$$\frac{dc^+}{dx} + c^+ \frac{d\varphi}{dx} = -j \quad (3.5)$$

$$\frac{dc^-}{dx} - c^- \frac{d\varphi}{dx} = 0 \quad (3.6)$$

$$\varepsilon_1^2 \frac{d^2\varphi}{dx^2} = c^- - c^+ \quad (3.7)$$

The dimensionless parameter ε_1^2 is equal to $2(\lambda_D/l)^2$. λ_D indicates the Debye length with the following formulation⁵⁰:

$$\lambda_D = \left(\frac{\varepsilon \varepsilon_0 k_B T}{2e^2 c_{\infty}} \right)^{1/2} \quad (3.8)$$

The dimensionless boundary conditions at the electrode and electroneutral bulk read:

$$x = 0, c^- = c^+ = 1, \varphi = 0 \quad (3.9)$$

$$x = 1, \varphi = -V_0 \quad (3.10)$$

Considering the domain length long enough so that $\lambda_D \ll l$ yields $\varepsilon_1^2 \ll 1$, which in itself makes the problem stated by Eqs. (3-5) to (3-7) singular. In distances from the cathode greater or equal to l , the left-hand side of Eq. (3.7) becomes negligible. Hence, full electroneutrality reveals at such distances. Adding this electroneutrality ($c^+ - c^- = 0$) to Eqs. (3.5) - (3.6) and integrating under the bulk boundary conditions (3.9), yields:

$$c^+ = c^- = 1 - \frac{j}{2}x \quad (3.11)$$

Integrating Eq. (3.6) with accounting the boundary conditions in (3.9) yields:

$$\varphi = \ln \left(1 - \frac{j}{2}x \right) \quad (3.12)$$

Equations (3.11) and (3.12) demonstrate the outer solution of the considered problem. The outer solution is well-known and reveals that the dimensionless cation flux does not exceed the value of $j=2$, which brings the cation concentration to zero as we approach the electrode (i.e., $x \rightarrow 1$)³⁷. This is related to the case of a strong faradaic reaction at the electrode surface where a diffusion-limited regime occurs. Our interest is the slow discharge regime governed by the Frumkin-Butler-Volmer equation^{35,36}, i.e., the cases with $j \ll 2$.

The outer boundary solutions, i.e. (3.11) and (3.12) are invalid in the inner boundary domain where there is polarization. In the inner boundary layer, the left-hand side of Eq. (3.7) is no longer negligible and, as mentioned earlier, makes the problem singular. A stretched coordinate should be employed to overcome the singularity^{51,52}. The stretched coordinate X can be defined as $X = (1 - x)/\varepsilon_1$ with X being in the order of 1. Neglecting the small term $\varepsilon_1 j$, (since $\varepsilon_1 \ll 1$) yields the following governing equations for the inner boundary layer:

$$\frac{dc^+}{dX} + c^+ \frac{d\varphi}{dX} = 0 \quad (3.13)$$

$$\frac{dc^-}{dX} - c^- \frac{d\varphi}{dX} = 0 \quad (3.14)$$

$$\frac{d^2\varphi}{dX^2} = c^- - c^+ \quad (3.15)$$

Figure (3.1) indicates a schematic of the inner and outer boundary layers with considered coordinates for each cathode and anode electrodes.

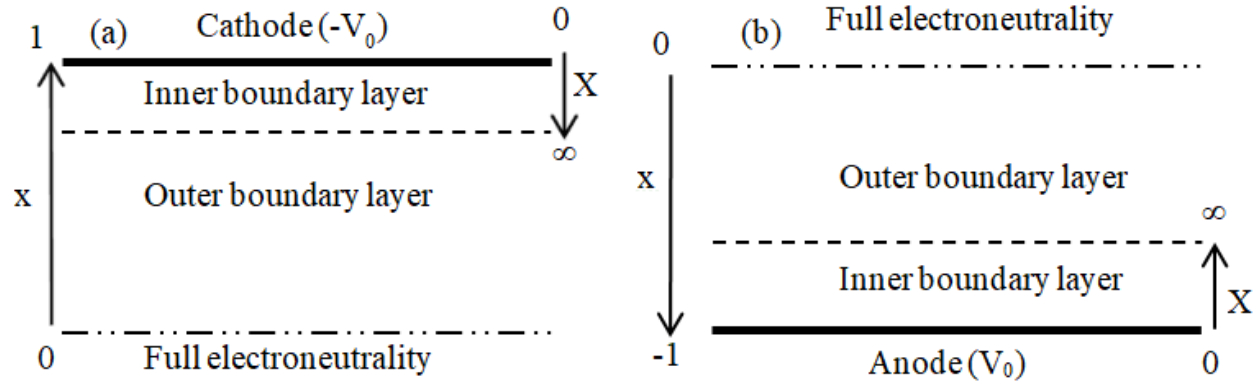


Figure 3.1. (a) The inner and outer boundary layers for a cathodic half-cell, (b) The inner and outer boundary layers for an anodic half-cell.

It is deduced from Eq. (3.15) that the inner boundary layer is polarized. Integrating Eqs. (3.13) and (3.14) provides

$$c^+ = K_1 \exp(-\varphi), c^- = K_2 \exp(\varphi) \quad (3.16)$$

with K_1 and K_2 being the constants of integration. These are found by matching with Eq. (3.11) as $X \rightarrow \infty$, while $x \rightarrow 1$ which gives:

$$K_1 = \left(1 - \frac{j}{2}\right)^2, K_2 = 1 \quad (3.17)$$

The inner solution for the ion concentrations becomes:

$$c^+ = \left(1 - \frac{j}{2}\right)^2 \exp(-\varphi), c^- = \exp(\varphi) \quad (3.18)$$

Replacing the solutions of (3.18) in Eq. (3.15) provides:

$$\frac{d^2\varphi}{dX^2} = \exp(\varphi) - \left(1 - \frac{j}{2}\right)^2 \exp(-\varphi) \quad (3.19)$$

In the limiting condition of small j and relatively small φ (and V_0), the linearization of Eq. (3.19) reads

$$\frac{d^2\varphi}{dX^2} - 2\varphi = j \quad (3.20)$$

The inner solution for the electric potential in general form becomes

$$\varphi = K_3 \exp(\sqrt{2}X) + K_4 \exp(-\sqrt{2}X) - \frac{j}{2} \quad (3.21)$$

K_3 and K_4 are the integration constants. In a similar limit of small j , the outer solution of electric potential reads

$$\varphi = -\frac{j}{2}x \quad (3.22)$$

By matching solutions (3.21) and (3.22) as $X \rightarrow \infty$, while $x \rightarrow 1$, we obtain $K_3 = 0$. Satisfying the boundary condition (3.10) for the inner solution gives $K_4 = (-V_0 + j/2)$. By replacing the integration coefficients in solution (3.21), we have the final form as

$$\varphi = (-V_0 + j/2) \exp(-\sqrt{2}X) - \frac{j}{2}, X = \frac{(1-x)}{\varepsilon_1} \quad (3.23)$$

It is interesting to note that the non-linear Eq. (3.19) accepts an order reduction. However, the concluding first-order equation does not have an analytical solution. It can be reformulated as a

second-order equation, which still has to be solved numerically. Hence, the non-linear boundary-layer problem in Eq. (3.19) should be dealt with numerically as a quadratic equation.

Equation (3.23) represents the ohmic limit of the faradaic reactions. It is important to note that in any circumstances (low-voltage ohmic or non-linear high-voltage regime), the electric current density J_e (rendered dimensionless by $eDc_{*\infty}/l$) is a function of applied voltage at the electrode $J_e = J_e(-V_0)$ governed by the Frumkin-Butler-Volmer equation^{35,36}.

The dimensionless charge density of the inner layer ($ec_{*\infty}$ as the scale) in the limit of small flux value j and electric potential φ reads

$$q = -2\varphi - j \quad (3.24)$$

With knowing the dependency of electric current density J_e on the applied voltage at the cathode $-V_0$, the electric potential and charge density inside the polarized inner layer can be fully determined. In the presence of a tangential electric field $E_{*\tau}$, an electro-osmotic flow could arise in the inner layer where polarization exists. The Smoluchowski velocity along the cathode $u_{*Sm} = -\varepsilon\varepsilon_0 E_{*\tau}(-V_{0*} - \varphi_*)/\mu$ in the dimensionless form becomes:

$$u = \varphi + V_0 \quad (3.25)$$

Here, the scales are $\varepsilon\varepsilon_0 k_B T E_{*\tau}/\mu e$ for the velocity and $c_{*\infty} \varepsilon\varepsilon_0 k_B T E_{*\tau} l/\mu$ for the electric potential with μ being the solvent dynamic viscosity.

The dimensionless spray current in the polarized layer is found from Eqs. (3.23) - (3.25) as:

$$j_{spray} = \int_0^\infty q u dX = \frac{(V_0 - j/2)^2}{\sqrt{2}} \quad (3.26)$$

which is made dimensionless by $c_{*\infty} \varepsilon\varepsilon_0 k_B T E_{*\tau} l/\mu$. The sign of dimensional spray current j_{*spray} can change with $E_{*\tau}$. For instance, in the case of a cathode $V_0 > 0$, $j > 0$ and $E_{*\tau} < 0$, we will have $j_{*spray} < 0$. For an anode with $V_0 < 0$, $j < 0$ and $E_{*\tau} > 0$, then, $j_{*spray} > 0$. The spray current

magnitude is the same in these cases for a symmetric 1:1 electrolyte with identical diffusion coefficients.

Similarly, the dimensionless governing equations for an anode subjected to a positive potential V_{0*} read:

$$\frac{dc^+}{dx} + c^+ \frac{d\varphi}{dx} = 0 \quad (3.27)$$

$$\frac{dc^-}{dx} - c^- \frac{d\varphi}{dx} = j \quad (3.28)$$

$$\varepsilon_1^2 \frac{d^2\varphi}{dx^2} = c^- - c^+ \quad (3.29)$$

Here, the flux j has the same magnitude as the cathode. Nevertheless, the motion of anions is in the opposite direction compared to the cations in the cathode case. The dimensionless boundary conditions for anodic half-cell are

$$x = 0, c^- = c^+ = 1, \varphi = 0 \quad (3.30)$$

$$x = -1, \varphi = V_0 \quad (3.31)$$

The anodic half-cell is depicted in Fig. (3.1) (b). The outer solution for the anode case is:

$$c^+ = c^- = 1 + \frac{j}{2}x \quad (3.32)$$

$$\varphi = -\ln\left(1 + \frac{j}{2}x\right) \quad (3.33)$$

For the anodic half-cell, the stretched coordinate becomes $X = (1 + x)/\varepsilon_1$. The near-anode inner layer solutions read

$$c^+ = \exp(-\varphi), c^- = \left(1 - \frac{j}{2}\right)^2 \exp(\varphi) \quad (3.34)$$

The governing equation for the electric potential in the inner layer is found as

$$\frac{d^2\varphi}{dX^2} = \left(1 - \frac{j}{2}\right)^2 \exp(\varphi) - \exp(-\varphi) \quad (3.35)$$

In the limit of small flux j and relatively small φ (and V_0), the linearized form of the Eq. (3.35) has the following analytical solution:

$$\varphi = (V_0 - j/2) \exp(-\sqrt{2}X) + \frac{j}{2} \quad (3.36)$$

The linearized solutions of (3.23) and (3.36) provide a benchmark case to be validated against the numerical solution of the non-linear equations (3.19) and (3.35).

3.2. The governing equations and the numerical methodology

The Open Field Operation and Manipulation (OpenFOAM) platform⁵³ has been used as the computational platform to build numerical tools. This library employs finite-volume-based schemes and boundary conditions written in a C++ standard template library. Two types of problems are considered, as discussed in the next sections.

3.2.1. Anodic half-cell without flow

The non-linear system of Eqs. (3.27) - (3.29) for an anodic half-cell are solved numerically by utilizing a smooth solver to validate the numerical predictions with the available inner and outer boundary layer solutions. An iterative approach with a run-time selected smoother (here the Gauss-Seidel) is employed to converge the residues to the required tolerance. A diagonal incomplete-Cholesky (DIC) preconditioner is employed to improve the convergence. The Cuthill-Mckee (CM) algorithm provides a band matrix of coefficients by renumbering the grid points⁵⁴.

3.2.2. Channel flow with the discharge of counter-ions in the middle section

The continuity and momentum equations of the incompressible flow with a source term in momentum equation accounting for the Coulombic body force in dimensional form read

$$\nabla \cdot \mathbf{V}_* = 0 \quad (3.37)$$

$$\rho_* \left[\frac{\partial \mathbf{V}_*}{\partial t_*} + (\mathbf{V}_* \cdot \nabla) \mathbf{V}_* \right] = -\nabla p_* + \mu \nabla^2 \mathbf{V}_* + q_* \mathbf{E}_* + q_* \mathbf{E}_{*ext} \quad (3.38)$$

with $q_* = e(c_*^+ - c_*^-)$ being the bulk charge density, $\mathbf{V}_*$ is the velocity vector, ρ_* indicates the fluid density, p_* marks the pressure and $\mathbf{E}_* = -\nabla\varphi_*$ is the electric field due to the gradient of electric potential inside the domain. $\mathbf{E}_{*\text{ext}}$ indicates the externally applied electric field vector. The last two terms in the momentum equation represent the source terms related to internal and external electric fields superimposed on each other.

The dimensional cation and anion transport equations along with the Poisson equation for the self-induced electric potential are

$$\frac{\partial c_*^+}{\partial t_*} + \nabla \cdot (c_*^+ \mathbf{V}_*) = D \nabla^2 c_*^+ + \frac{De}{k_B T} \nabla \cdot (c_*^+ \nabla \varphi_*) \quad (3.39)$$

$$\frac{\partial c_*^-}{\partial t_*} + \nabla \cdot (c_*^- \mathbf{V}_*) = D \nabla^2 c_*^- - \frac{De}{k_B T} \nabla \cdot (c_*^- \nabla \varphi_*) \quad (3.40)$$

$$\nabla^2 \varphi_* = -\frac{q_*}{\varepsilon \varepsilon_0} \quad (3.41)$$

The measured¹⁷ electric conductivity of the canola oil is $\sigma = 2.6 \times 10^{-11} \text{ S/m}$ with the dielectric permittivity of $\varepsilon = 3$. This yields the charge relaxation time as $\tau_C = \varepsilon \varepsilon_0 / \sigma = 1 \text{ s}$. The diffusion coefficient is considered⁵⁵ to be $D = 10^{-11} \text{ m}^2/\text{s}$. By replacing charge relaxation formulation in Eq. (3.8) and considering the electric conductivity formulation as $\sigma = 2 \frac{De^2}{k_B T} c_{*\infty}$, the Debye length becomes $\lambda_D = (D\tau_C)^{1/2}$ which gives $\lambda_D = 3.16 \text{ }\mu\text{m}$. The bulk ion concentration calculated from Eq. (3.8) will be in the order of 10^{17} 1/m^3 for the canola oil.

3.3. Results and Discussion

Here, the numerical prediction for an anodic half-cell case without flow is considered and validated against the benchmark boundary layer solution of section (3.2). Afterward, an electrohydrodynamic microchannel flow is predicted and validated versus the available benchmark data. Next, another microchannel with liquid charging by the electrode faradaic reactions is studied numerically.

3.3.1. Numerical solution for the anodic half-cell without flow

Two one-dimensional cases are studied to validate the numerical solutions of Eqs. (3.39) - (3.41) against the analytical solutions provided in relations (3.32) - (3.36). In the first case, the applied electric potential at the electrode and the corresponding species flux values at the electrode surface are taken independent of each other (i.e., unrelated by the Frumkin-Butler-Volmer kinetics). In the second case, the relation between the applied electric potential and the counter-ion flux is found from the experimental measurements¹⁷ associated with the low-voltage limit of the Frumkin-Butler-Volmer equation.

In the first case, the applied electric potential at the anode V_0 , anions flux j , and the dimensionless parameter ε_1 are selected as $V_0 = 0.0012$, $j = 0.002$ and $\varepsilon_1 = 10^{-3}$. Figure (3.2) provides a comparison between the numerical predictions and analytical solutions across the anodic half-cell domain (cf. Fig. (3.1)(b)).

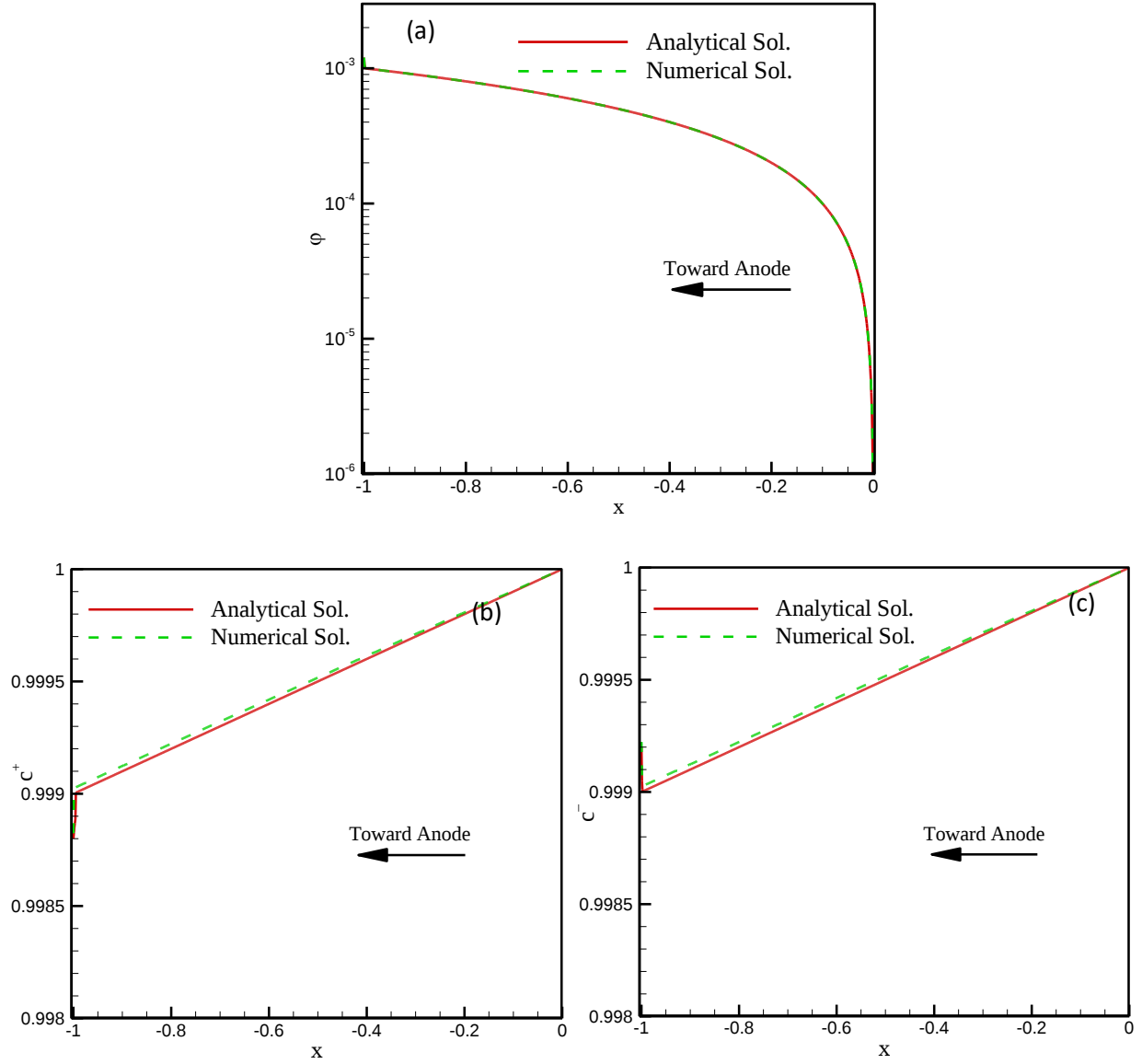


Figure 3.2. Comparison of the numerically predicted distributions with the analytical solutions for the anode half-cell. (a) Electric potential distribution, (b) cation concentration and (c) anion concentration.

The comparison reveals that the numerical predictions are in perfect agreement with the analytical solutions. It is interesting to note that the numerical predictions can capture the abrupt slope change in the vicinity of the anode related to the anions and cations concentration. This is

obvious in Figs. (3.2) (b)-(c). To provide a better comprehension of circumstances in the vicinity of the electrode, the distributions in this region are magnified and depicted in Fig. (3.3).

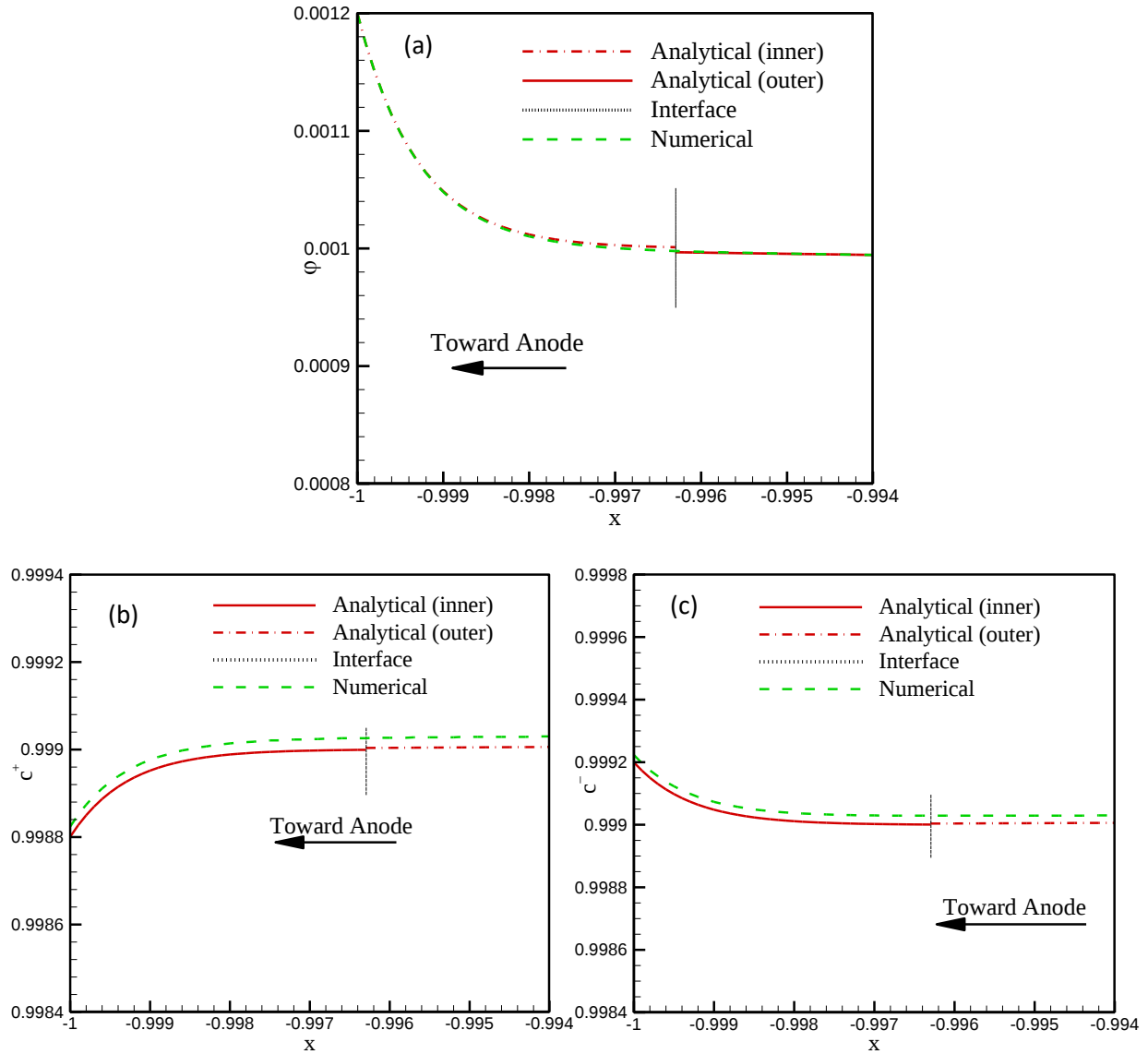


Figure 3.3. Zoomed-in views of the anode boundary layer and the asymptotical matching zone, which is marked by vertical dotted lines. (a) Electric potential distribution, (b) cation concentration and (c) anion concentration. It is emphasized that (b) and (c) do not show any systematic error. By a tremendous stretching of the vertical axes, it is always possible to separate two non-identical lines (asymptotically approaching each other) at a certain axis stretching, as is the case here.

It should be emphasized that the observed difference between the numerical predictions and analytical solutions in Fig. (3.3) is due to the extreme stretch of the vertical axis. Otherwise, the error is entirely negligible. The zoomed-in and whole-domain predictions perfectly depict the matching of inner and outer boundary layer solutions and the accurate spanning of the entire domain by the numerical predictions.

In the second validation case considered in the present subsection, the limiting low-voltage dependency of electric current density and applied voltage at the electrode follows the Frumkin-Butler-Volmer equation and is measured as¹⁶:

$$J_{e*} = 10^{-4.43} \times 38.66V_{0*} \left[\frac{A}{m^2} \right] \quad (3.42)$$

By choosing a small value of 2×10^{-12} V for the anode potential, we obtain the corresponding electric current density as 2.87×10^{-15} A/m². The ϵ_1 value is 10^{-3} as the previous one-dimensional validation case. Hence, the corresponding dimensionless flux of ions is calculated to be $j = 3.74 \times 10^{-5}$. Figure (3.4) demonstrates the distribution of electric potential and ion concentration over the entire domain $-1 < x < 0$. Once again, the agreement of the asymptotic analytical and numerical solutions is reasonably good.

The magnified views of the near-anode inner layer and the matching zone in the case corresponding to the low-voltage limit of the Frumkin-Butler-Volmer kinetics for canola oil are indicated in Fig. (3.5).

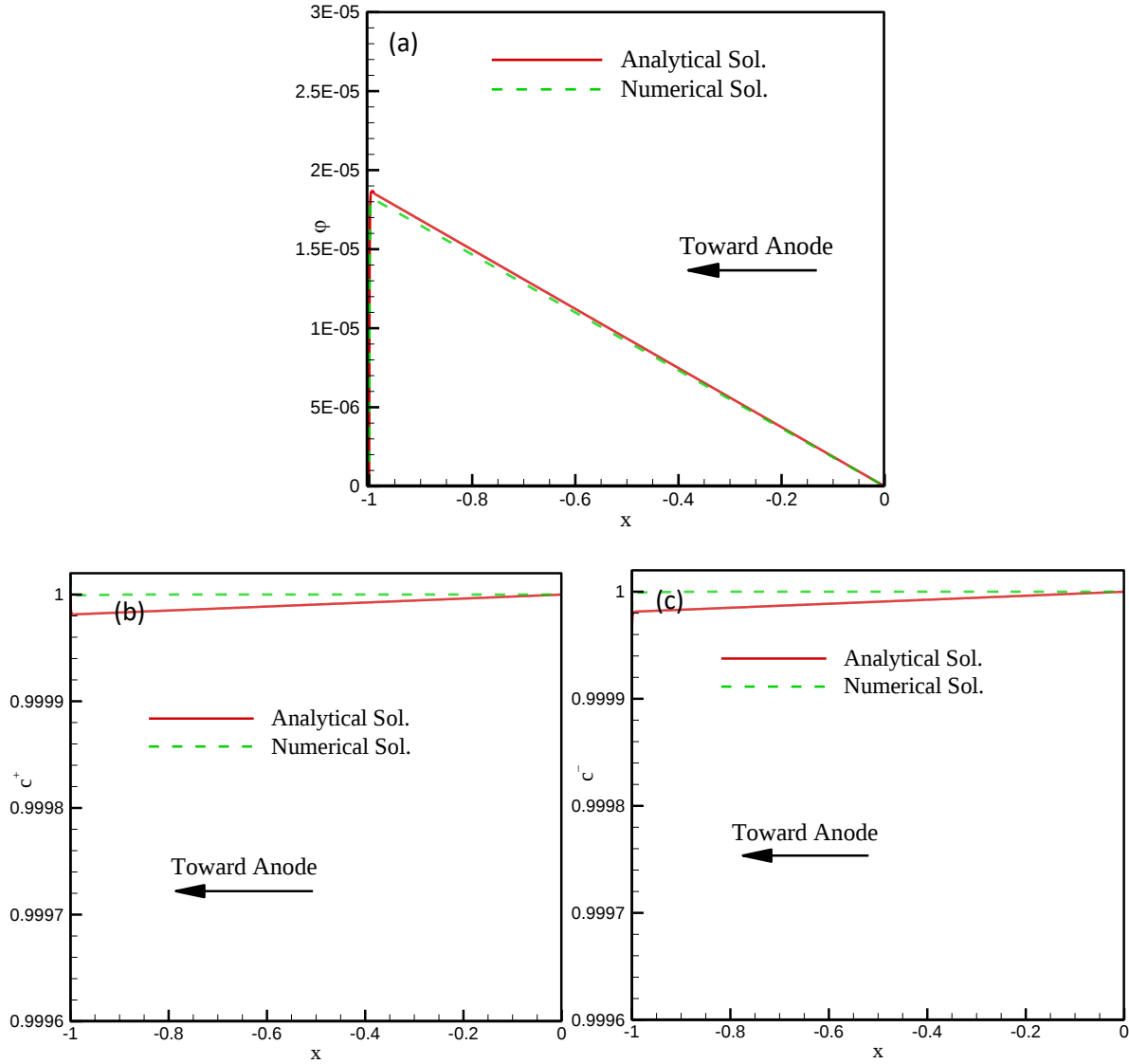


Figure 3.4. Comparison of the numerically predicted electric potential and ion concentration distributions with the benchmark analytical solution in the case corresponding to the low-voltage limit of the Frumkin-Butler-Volmer kinetics measured for canola oil¹⁴. (a) Electric potential distribution, (b) cation concentration and (c) anion concentration.

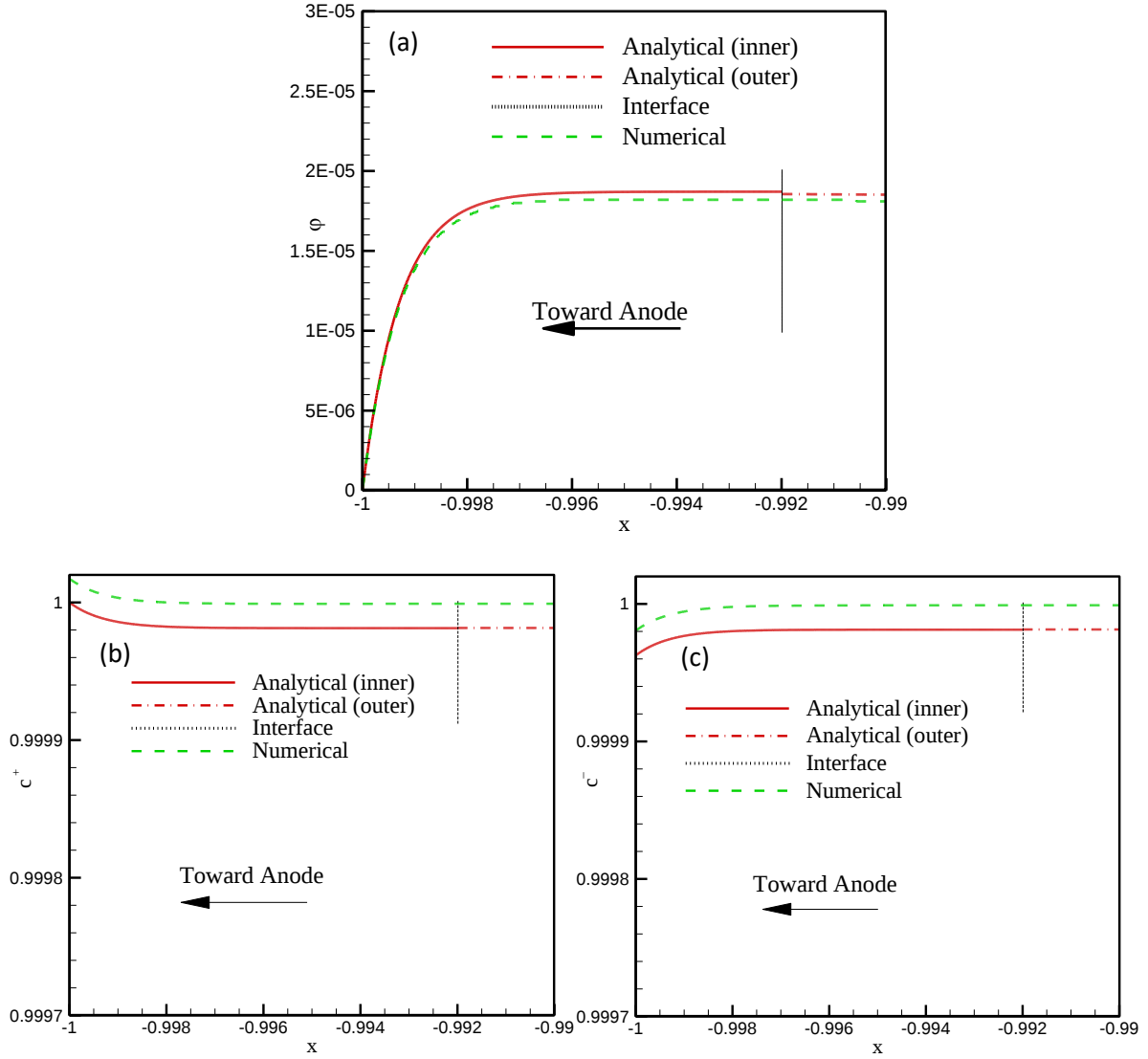


Figure 3.5. Zoomed-in views of the near-anode boundary layer and the asymptotical matching zone, which is marked by vertical dotted lines. The low-voltage limit of the Frumkin-Butler-Volmer kinetics for canola oil¹⁴. (a) Electric potential distribution, (b) cation concentration and (c) anion concentration.

3.3.2. Electro-osmotic flow

3.3.2.1. Two-dimensional validation case

A two-dimensional planar microchannel flow driven by the pressure gradient and electro-osmotic component associated with a polarizing dielectric section (cf. Fig. (3.6)), which possess a non-zero ζ -potential is studied numerically. The microchannel imposes a non-zero ζ -potential in the middle section and has an analytical solution¹²⁻¹³. The inlet flow field is assumed to be fully developed and steady with no-slip boundary condition throughout the channel.

The analytical one-dimensional velocity profile in the middle section of the microchannel (driven by pressure and electro-osmotic flow) is given as¹²⁻¹³:

$$u(y) = -\frac{1}{2} \frac{dp}{dx} (1 - y^2) + 1 - \varphi(y) \quad (3.43)$$

where x and y are the dimensionless Cartesian coordinates, p is the dimensionless pressure, φ marks the dimensionless electric potential, and u is the dimensionless velocity, neglecting dependence on x . This distribution serves as a plausible approximation for the middle polarizing section of the channel drawn in Fig. (3.6).

The scales used to provide dimensionless parameters are the half-channel height h_* for x_* and y_* , the ζ -potential for φ_* , $\mu u_s/h_*$ for p_* , and $-\varepsilon \zeta E_{*ext}/\mu$ for u_* . Here, $u_{*Sm} = -\varepsilon \zeta E_{*ext}/\mu$ is the Smoluchowski velocity with E_{*ext} being the externally applied electric field in the spanwise direction.

The microchannel is constituted of three parts, with the middle section having dielectric polarizing walls with the dimensionless potential being $\varphi = 1$. The entry and exit sections are non-polarizing with $\varphi = 0$. Each section has the dimensionless length $L=3.1$. h_* is chosen to be $6 \mu\text{m}$. The Debye length is 30 nm (the case of an aqueous solution, as in Ref. 13). The polarized layer thickness is considered to be constant along the electrode section.

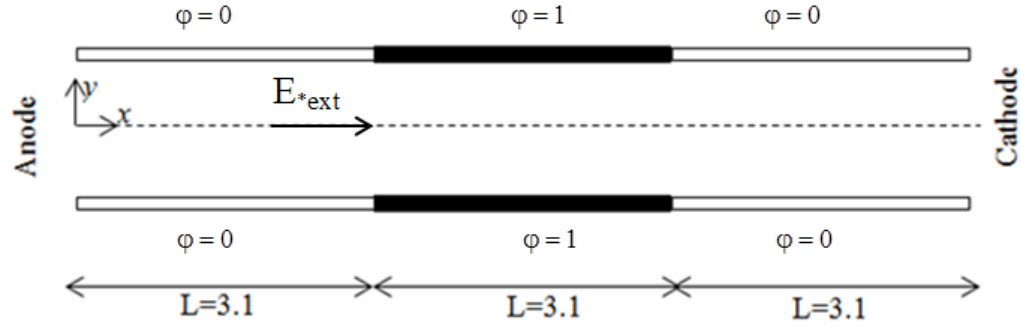


Figure 3.6. Configuration of a microchannel with electro-osmotic/pressure-driven flow. The electro-osmotic force is associated with two polarizing dielectric middle sections (shown with thick black lines), which possess a non-zero ζ -potential.

The Reynolds number of the fully-developed inflow is 0.005 (calculated based on the average inflow velocity and h_*). The ζ -potential at the polarized section is considered to be $\zeta = -25.4$ mV. The longitudinal electric field strength is constant. The analytical solution of the one-dimensional Poisson equation yields the electric potential distribution near the polarizing sections¹³:

$$\frac{d^2\phi}{dy^2} = \beta \sinh(\alpha\phi) \quad (3.44)$$

Here, α and β are the dimensionless parameters with values, 1 and 10000, respectively¹³. Table (3.1) lists the Smoluchowski velocity values related to the applied external electric field strengths. It also shows the dimensionless maximum velocity values corresponding to a fixed dimensional velocity of $u_{*in} = 0.0025$ m/s in these cases.

Table 3.1. The Smoluchowski velocity for several external longitudinal electric field strengths.

$E_{*ext}(\text{V/m})$	$u_{*Sm}(\text{m/s})$	$u_{*in}(\text{m/s})$	$u_{in}(\text{m/s})$
6.950×10^4	0.00125	0.0025	2

9.392×10^4	0.00168	0.0025	1.485
1.390×10^5	0.0025	0.0025	1

The numerically predicted dimensionless velocity profile at $x = 4.5$ (lies within the middle polarizing section) is compared with the analytical solution (3.43) in Fig. (3.7). As can be seen, the numerical predictions and analytical solutions are in good agreement despite the fact that the analytical solution neglects the two-dimensional character of the flow. A grid resolution study is performed to indicate the grid independence of the numerical findings. The grid specifications are displayed in Table (3.2).

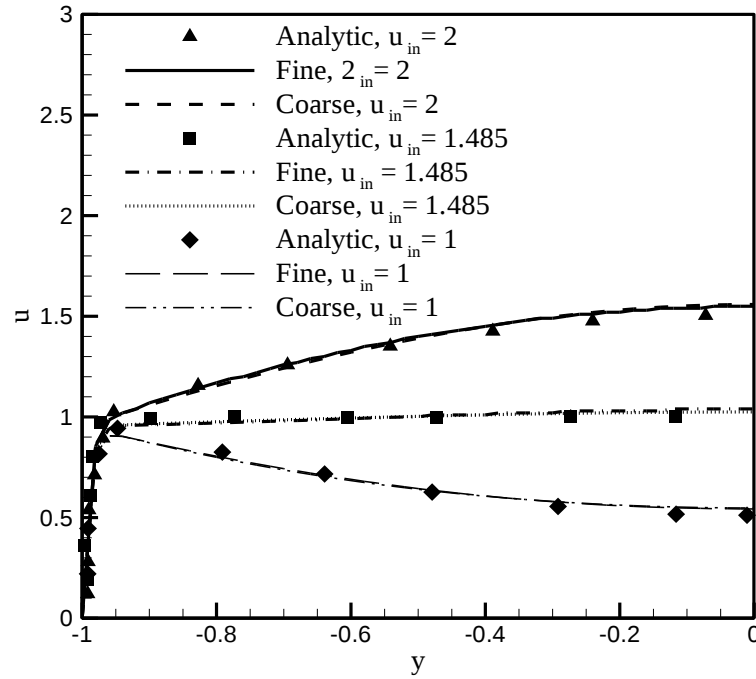


Figure 3.7. Comparison of the numerically predicted and analytical dimensionless velocity profiles at $x = 4.5$ (in the polarizing section). The results for half-channel $-1 \leq y \leq 0$ are shown.

Table 3.2. Grid specification used in the simulations.

Cell Dimensions	Δx	Δy_{wall}	Δy_{center}	Total points
Coarse Grid	0.0197	0.00383	0.0077	328042
Fine Grid	0.0123	0.0033	0.0066	632342

Figure 8 depicts the predicted dimensional axial velocity component for the external electric field strengths of $E_{*ext} = 1.390 \times 10^5$ and 6.950×10^4 V/m. It is seen that the two-dimensional distribution of the flow field (due to the existence of the polarizing middle section) is not addressed by the simplified analytical solution (3.43). The strong Coulombic body force due to the externally applied electric field and polarized section completely changes the initially Poiseuille-like velocity profile in the middle part, moving the high-velocity region toward the polarizing walls.

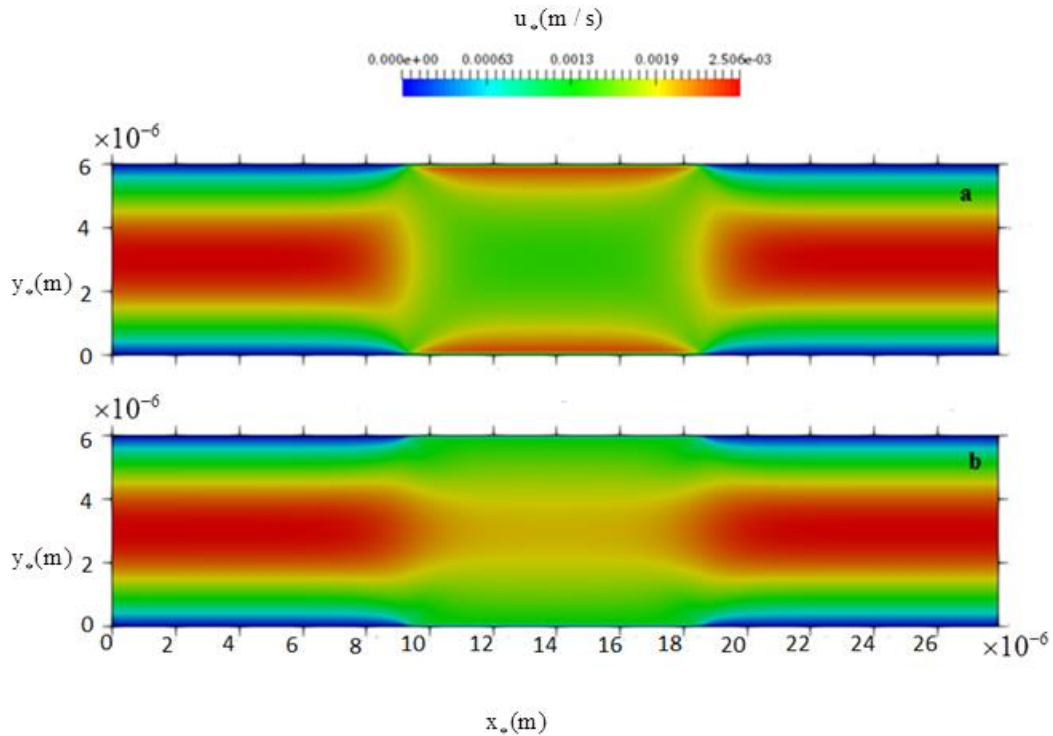


Figure 3.8. Predicted fields of the axial velocity component for externally applied electric field strengths of (a) $E_{*ext} = 1.390 \times 10^5$ V/m and (b) $E_{*ext} = 6.950 \times 10^4$ V/m.

3.3.2.2. Numerical modeling of liquid electrification and transport in a microchannel flow

Here, we consider another microchannel composed of three sections, the entry, middle, and exit sections. An active middle electrode section, as depicted in Fig. (3.9), replaces the polarizing one of Fig. (3.6). The entry and exit sections are electrically insulated and do not sustain any electric current due to faradaic reactions. The entry and the electrode sections are 6 μm long, whereas the exit section is 96 μm . The channel height is 20 μm . The inflow is a fully developed Poiseuille flow with the maximum velocity of $u_{\text{in}} = 0.00385 \text{ m/s}$. The Reynolds number, defined based on the half-channel height and the maximum inlet velocity, is 4.9×10^{-4} . The bulk ion concentration is $8 \times 10^{17} \text{ 1/m}^3$ (based on Eq. (3.8)).

The no-slip conditions are imposed at the channel wall throughout the entire length. The inlet and the exit section walls do not sustain any faradaic reactions (i.e., are fully insulated) or any non-specific adsorption. Accordingly, the cation and anion fluxes $j_*^\pm$ at the walls of these sections vanish, i.e., $\partial c_*^\pm / \partial y_* = \partial \varphi_* / \partial y_* = 0$. On the other hand, the electrodes sustain faradaic reactions and carry electric current due to the attached battery (Fig. 3.9). The normal to the wall components of the ion fluxes at the walls, where the convective ion transport vanishes, are given by

$$j_*^\pm = -D \frac{dc_*^\pm}{dy_*} \mp \frac{De}{k_B T} c_*^\pm \frac{d\varphi_*}{dy_*} \quad (3.44)$$

The cations flux at the anode surface (the upper electrode in Fig. (3.9)) is zero, whereas at the cathode surface it is determined as j_*^+ , namely

$$\frac{dc_*^+}{dy_*} = -\frac{e}{k_B T} c_*^+ \frac{d\varphi_*}{dy_*} \quad (\text{anode}) \quad (3.45)$$

$$\frac{dc_*^+}{dy_*} = -\frac{j_*^+}{D} - \frac{e}{k_B T} c_*^+ \frac{d\varphi_*}{dy_*} \quad (\text{cathode}) \quad (3.46)$$

Similarly, the boundary conditions associated with the anions at the electrodes are:

$$\frac{dc_*^-}{dy_*} = -\frac{j_*^-}{D} + \frac{e}{k_B T} c_*^- \frac{d\phi_*}{dy_*} \quad (\text{anode}) \quad (3.47)$$

$$\frac{dc_*^-}{dy_*} = \frac{e}{k_B T} c_*^- \frac{d\phi_*}{dy_*} \quad (\text{cathode}) \quad (3.48)$$

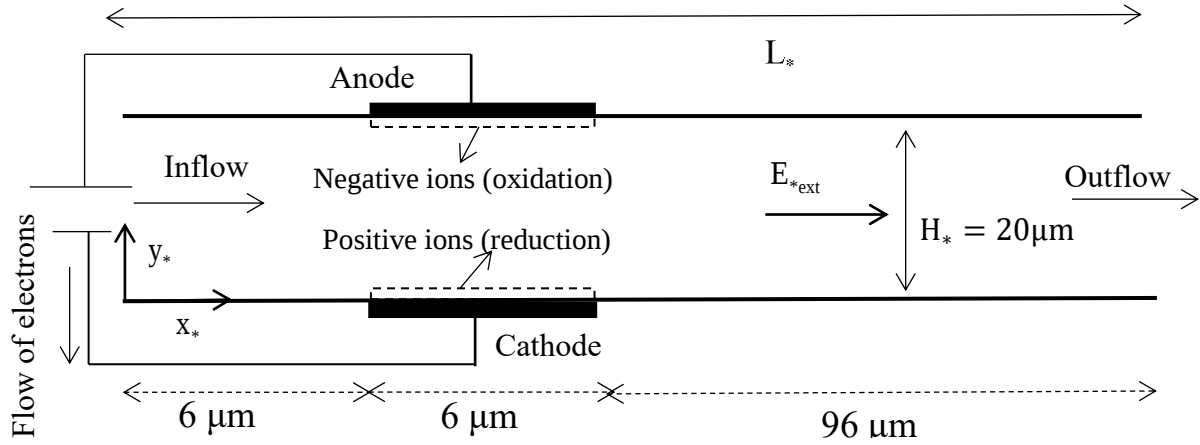


Figure 3.9. Microchannel with the two opposite polarity electrodes used to charge liquid in throughflow. The externally applied electric field is in the longitudinal (x_*) direction.

Inside the electrostatic atomizers, the ionic conductor liquid flows through an electrode section and faradaic reactions generate a net charge that can be carried (mostly through convection) toward the counter-electrode (typically, ground¹⁶⁻¹⁷). The free jet exiting the atomizer is sustained by a pump (pressure-driven) and is uncoupled from electric pulling toward the counter-electrode.

It should be emphasized that $|j_*^+| = |j_*^-|$, and the applied voltages at the electrodes are ± 500 V. The experimentally derived¹⁷ current-voltage relation for the cathode in this case is as follows:

$$J_{e*} = j_{0*} 10^{[(-V_{0*}/2 + \psi_1)/b_c]} = 10^{[-V_{0*}/2 - (a_c - \psi_1)]/b_c} \left[\frac{\text{A}}{\text{cm}^2} \right] \quad (3.49)$$

where j_{0*} indicates the exchange current density, $-V_{0*}/2$ is the applied electric potential at the cathode, $a_c - \psi_1$ and b_c are the experimental coefficients measured to be -29183.0 V and -3451.85 V, respectively. Equation (3.42) is the low-voltage limit of Eq. (3.49). By utilizing Eq. (3.49) and considering $-V_{0*}/2 = -500$, the value of electric current density at the cathode becomes 5.03×10^{-5} A/m² which in itself yields the flux of counter-ions at the electrodes to be $|j_*^+| = |j_*^-| = J_{e*}/e = 3.13 \times 10^{14}$ (m²s)⁻¹. Here and hereinafter, $\pm\psi_1$ denote the value of the electric potential at the interface of the compact²⁷ and diffuse layer on each electrode side (negative sign relates to the cathode and positive sign is associated with the anode). The inclusion of the Frumkin-Butler-Volmer equation (3.49) as a boundary condition for the system of the electrokinetic equations makes the present approach similar to that of Refs. 40 and 56.

Attached to each electrode, there is a thin compact layer²⁷. Stern proposed the first model for the compact layer, which was the case of a polarized layer created adjacent to a dielectric surface with a non-zero ζ -potential with no sustained electric current. Stern associates compact layer creation with non-specific (non-electric) adsorption/desorption equilibrium of ions at the surface⁴². Hence, it can also be constituted at the surface of conductive metallic electrodes without discharge of ions, i.e., at the insulating stains or oxide islands. Typically, an effective thickness λ_S is associated with the potential drop across the compact layer. In the case of the cathode, this general relation becomes^{40,42}:

$$\lambda_S \left. \frac{\partial \varphi_*}{\partial y_*} \right|_{\text{compact layer}} = -\frac{V_{0*}}{2} + \psi_1 \quad (3.50)$$

In the present numerical simulations of microchannel electrohydrodynamic flow, the reasonable value of $\lambda_S = 26.6$ nm provides the potential drop over the compact layer from $-V_{0*}/2 = -500$ to $-\psi_1 = -5$ V. The computational domain starts from the interface of the

compact and diffuse layers, adopting the characteristics of the compact layer. This removes the necessity for a prohibitively superfine grid to capture the steep gradients of electric potential and ionic concentration across the compact layer.

Table 3.3. Grid specifications for the simulations of microchannel charging of liquid (canola oil) in throughflow. The number of elements in the x and y directions and the total number of the elements are denoted as n_x , n_y and n_{tot} , respectively.

Δx_* (nm)	Δy_{*wall} (nm)	$\Delta y_{*center}$ (nm)	n_x	n_y	n_z	n_{tot}
67	3.9	78	1620	800	2	2,592,000
60	3.4	69	1800	900	2	3,240,000

The canola oil, as mentioned earlier, is the flowing liquid¹⁷. The temperature is taken as 300 K. The kinematic viscosity of canola oil is measured⁵⁷ to be $7.82 \times 10^{-5} \text{ m}^2/\text{s}$. The effect of externally applied electric field on the transport of ions (and charges) along the microchannel is also studied. Two different computational grid resolutions are considered, and it is seen that further refinement in both spanwise and crosswise directions will not affect the provided results.

Figure (3.10) depicts the two-dimensional contours of ions within the computational domain. Strong repulsion of co-ions (blue color) and slight aggregation of counter-ions (red color in the zoomed-in view) can be seen in the figure. The accumulation of counter-ions can be interpreted as the outcome of competition between the discharge of counter-ions due to the faradaic reactions and attraction as a result of the strong electromigration term.

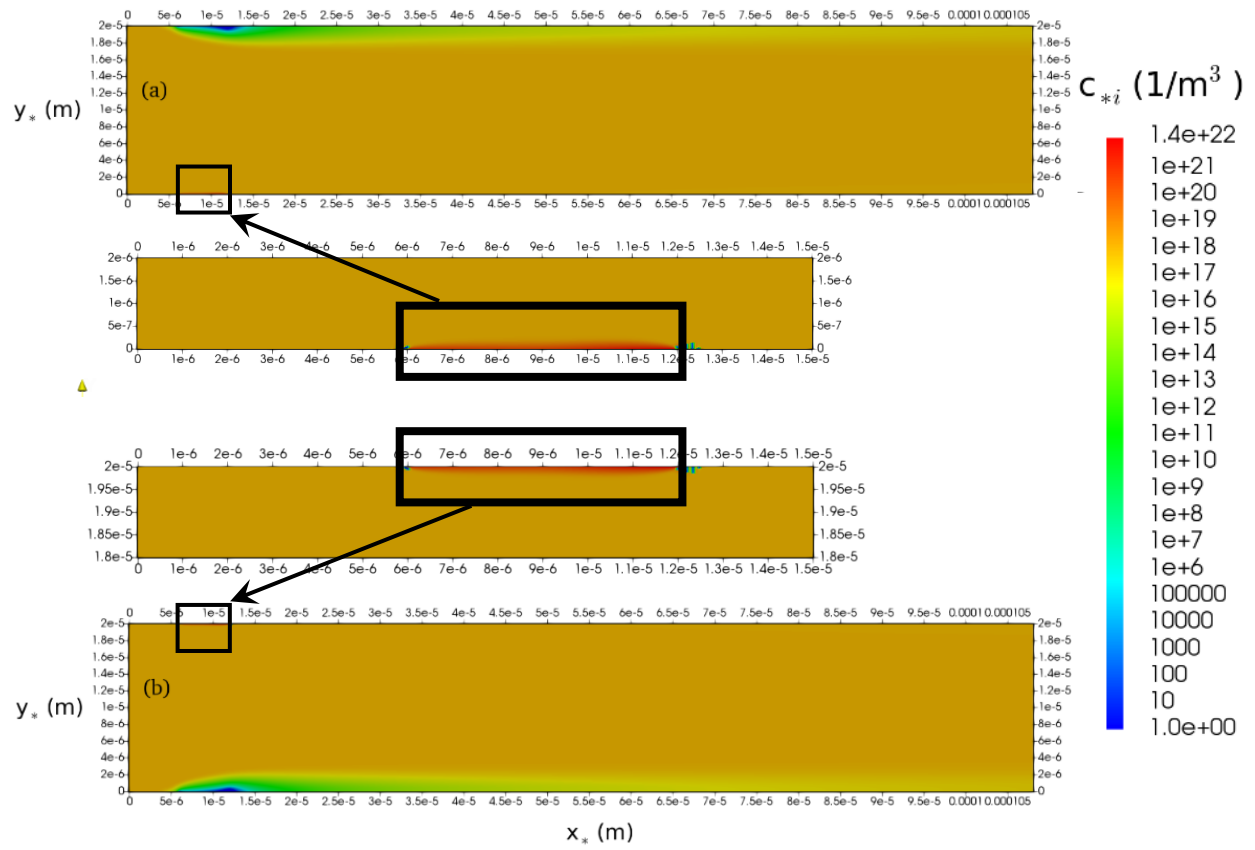


Figure 3.10. Two-dimensional contours of ions in the electrohydrodynamic flow of canola oil inside a microchannel exposed to opposite-polarity electrodes. (a) Cation concentrations and (b) anion concentrations.

The spanwise distribution of cation concentration at different vertical positions is demonstrated in Fig. (3.11). The scales are the half-channel height ($H_*/2$) for the coordinates (x_*, y_*) and bulk ion concentration ($c_{*\infty} = 8 \times 10^{17} \text{ m}^{-3}$) for the ion concentrations. At $y=0.03$ and for the locations inside the electrode section, an enhancement in the cation concentration arises. This signifies that the attraction of cations through the electromigration process is greater than the discharge of cations through faradaic reactions. At bottom-half, i.e., $y \in \{0.03, 0.2\}$ and downstream locations, the cation concentration tends to reduce. This reduction is associated with the crosswise diffusion of cations from the lower half toward the upper half of the microchannel.

Diffusion is inclined to evenly distribute the cation concentration in the exit part of the microchannel. The same suggestion justifies the gradual increase of cation concentration close to the upper wall of the microchannel ($y=1.97$). The strong repulsion of cations from the upper electrode (anode) is apparent in Fig. (3.11) (c), which reveals a region deprived of cations even after the electrode section up to $x=3$ locations.

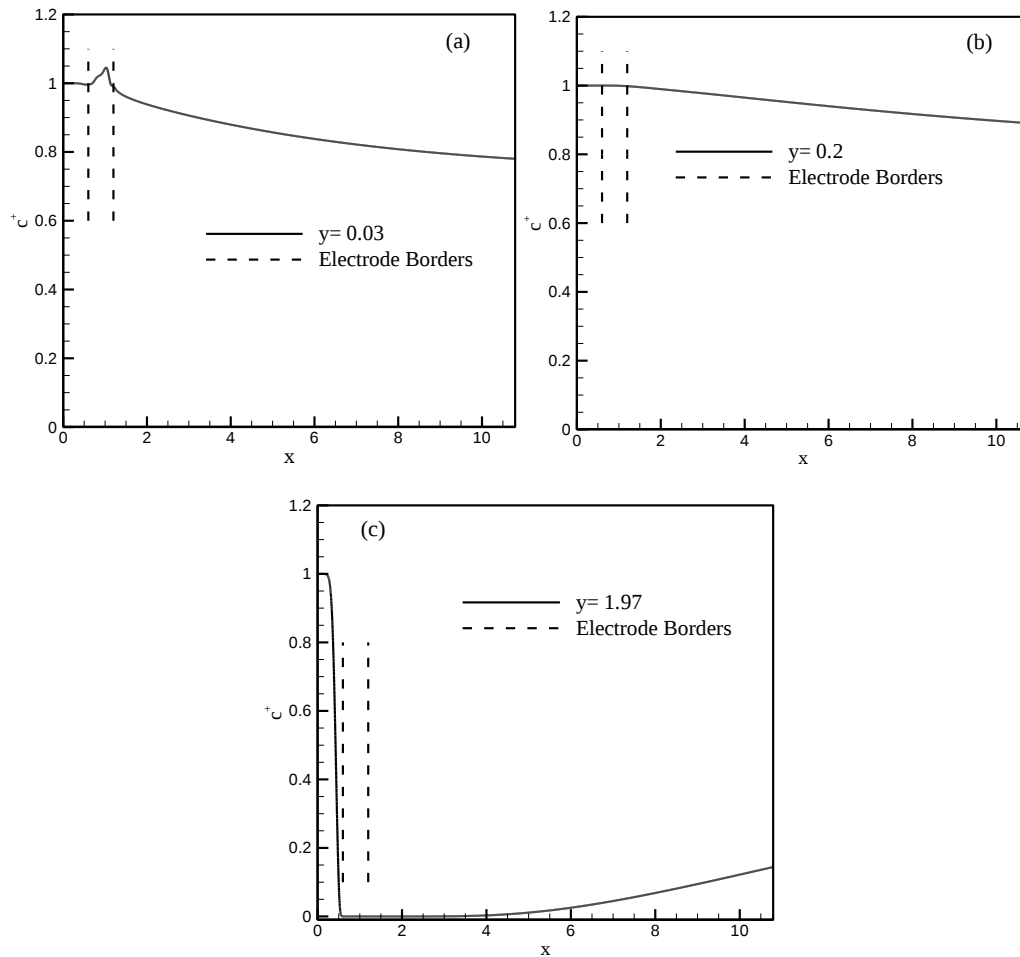


Figure 3.11. Dimensionless cation concentration along the channel and in different vertical positions. (a) $y=0.03$, (b) $y=0.2$, (c) $y=1.97$.

To verify that the ion transport equations are balanced numerically, the cation transport equation is used as an example. The terms of Eq. (3.39) at two different microchannel cross-sections are plotted in Fig. (3.12). One position lies within the middle electrode section, and the other one is far downstream. Here, there is no externally applied electric field. The cation transport equation terms including the time derivative $\partial c_*^+ / \partial t_*$, the convective $\nabla \cdot (c_*^+ \mathbf{V}_*)$, the electromigration $(De/k_B T) \nabla \cdot (c_*^+ \mathbf{V}_*)$ and the diffusive term $D \nabla^2 c_*^+$ are rendered dimensionless with the scale $\tau_c / c_{*\infty} = (8 \times 10^{17})^{-1} [\text{m}^3 \text{s}]$. The dimensionless residue represents the difference of the summation of right-hand side terms from the left-hand side ones. The zero values of the residue verify the numerical balance of cation transport equation terms.

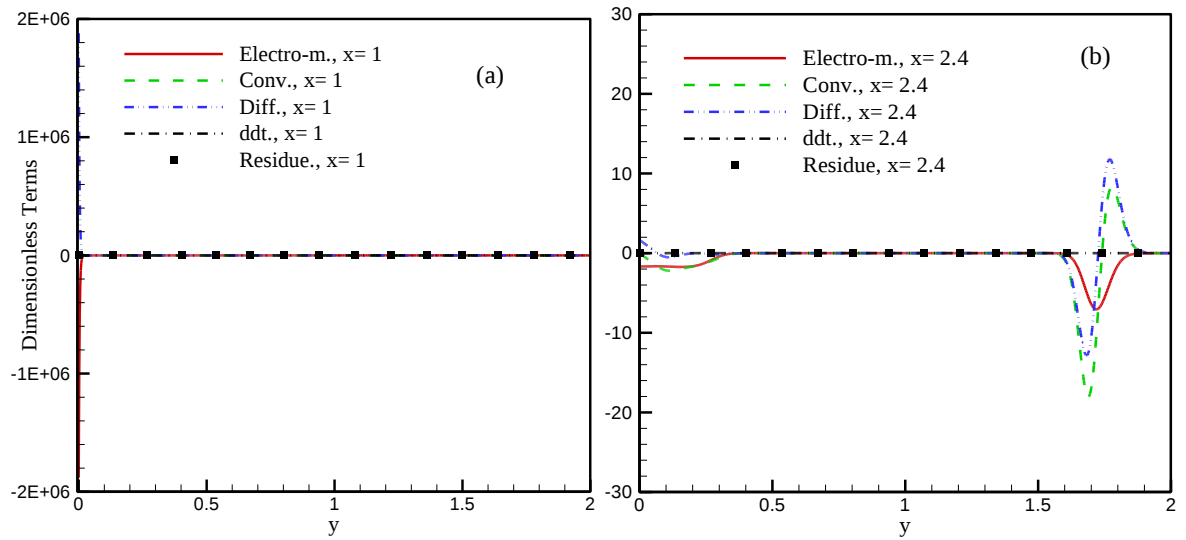


Figure 3.12. Dimensionless terms of the cation transport equation (3.3) at two cross-sections of the microchannel: (a) $x=1$ (inside the electrode section), (b) $x=2.4$ (far downstream from the electrode section). The figure legends are $\text{ddt.} = \partial c_*^+ / \partial t_*$, $\text{Diff.} = D \nabla^2 c_*^+$, $\text{Conv.} = \nabla \cdot (c_*^+ \mathbf{V}_*)$, $\text{Electro-m.} = (De / k_B T) \nabla \cdot (c_*^+ \nabla \phi_*)$.

Figure (3.12) indicates that inside the electrode section ($x=1$) and close to the electrode ($y \rightarrow 0$), the electromigration and diffusion terms become dominant. However, by moving away from the electrode in the y -direction, these terms deteriorate abruptly. This prediction is in agreement with the analytical boundary layer solution provided in section (3.2) in which the convective term is neglected at the electrode surface. The substantial values of the electromigration term at the electrode surface are attributed to the steep gradients of the electric potential in the perpendicular direction. At far downstream locations ($x=2.4$), the dominant terms are the convective and diffusive ones, representing the strong spanwise diffusion and convection in the after-electrode (exit) section. However, it is essential to note that the magnitude of the transport terms is much greater in the electrode section compared to the after-electrode downstream locations.

We consider the normal distance from the interface of the compact and diffuse layers to the position where the absolute net charge drops to 1% of the interface value, i.e., $0.01e(c_*^+ - c_*^-)|_{\text{int}}$, as the thickness of the diffuse layer (λ_d). Figure (3.13) reveals the thickness of the diffuse layer along the lower-half electrode (cathode). Similar distribution with equal values is expected along the upper-half electrode (anode). The observed concave curvature results from the electrode section border edges and the insulating walls on the diffuse layer profile. It is anticipated to observe a more flattened profile by increasing the length of the electrode section with respect to the insulating walls.

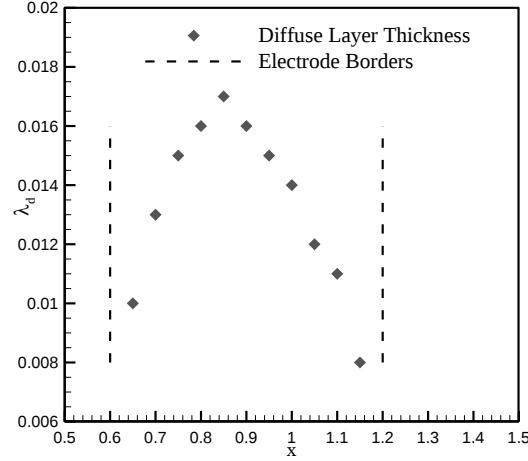


Figure 3.13. Diffuse layer thickness inside the electrode section (lower half) for the two-dimensional microchannel flow case

Figure (3.14) demonstrates the crosswise dimensionless distribution of ions at three spanwise locations. Two positions are selected inside the middle electrode section, and one position is far downstream. Here, we investigate the presence of an externally applied electric field on the transport of ions within the electrode section and in downstream locations. The magnitude of the external electric field is in the range observed in electrostatic atomizers¹⁷. Here, the thickness of the diffuse layer is found to be 172 nm.

It should be emphasized that based on Fig. (3.14), the exit section of the channel must be much longer than the current case to let the y -component of the diffusive term play a major role. In the current case, the convective and the x -component of the diffusive term carry the charge along the microchannel.

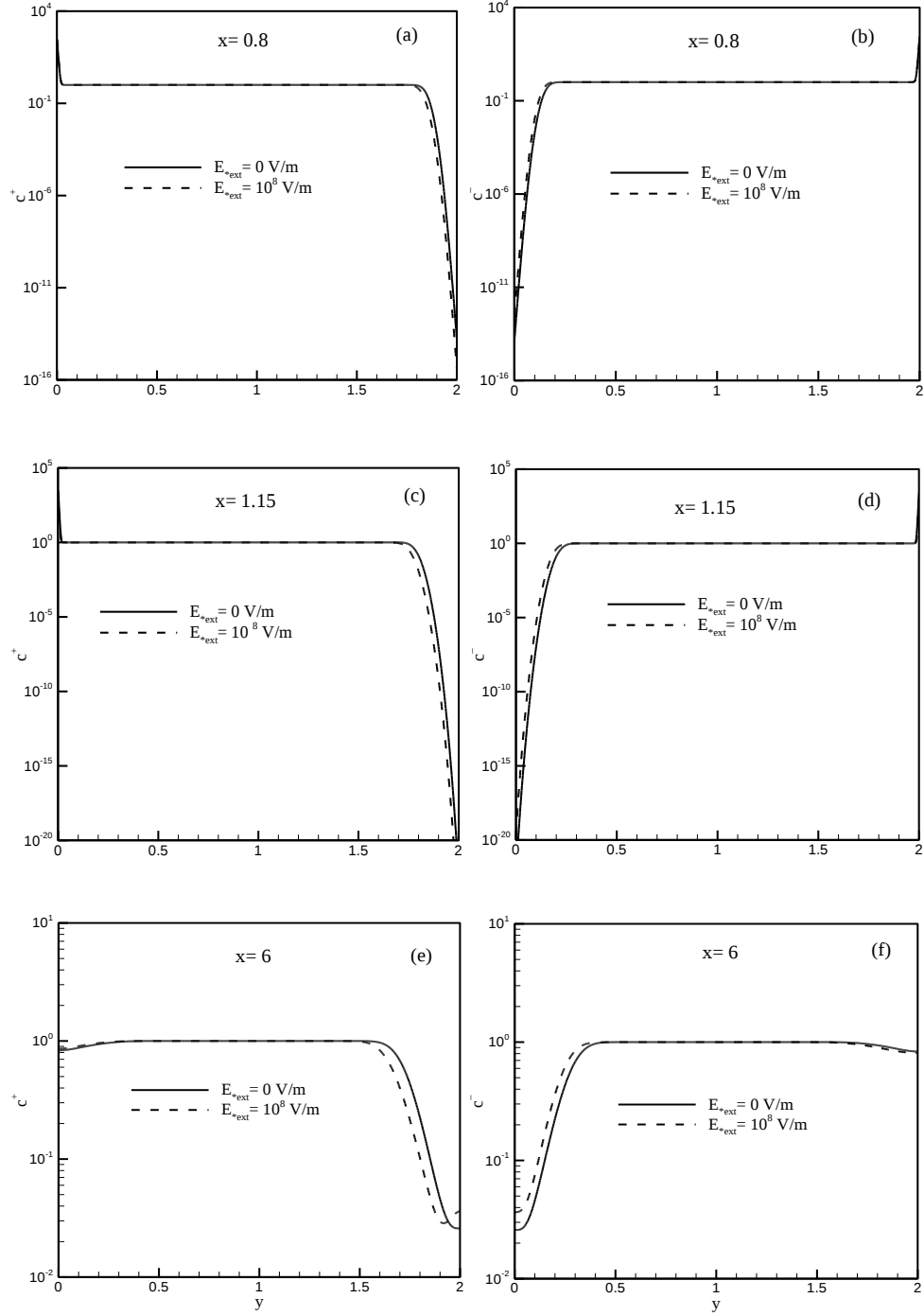


Figure 3.14. Distributions of ions within the electrode section and at the downstream location for two cases with and without an externally applied longitudinal electric field. (a) Cation concentration at $x=0.8$, (b) anion concentration at $x=0.8$, (c) cation concentration at $x=1.15$, (d) anion concentration at $x=1.15$, (e) cation concentration at $x=6$, (f) anion concentration at $x=6$.

The cross-sectional dimensionless average of the ion concentrations (which can be calculated as $\bar{c}_i = \int_0^1 c_i dy$) are indicated in Fig. (3.15) for the lower half of the channel. The distributions in the upper half of the channel are antisymmetric due to the geometry.

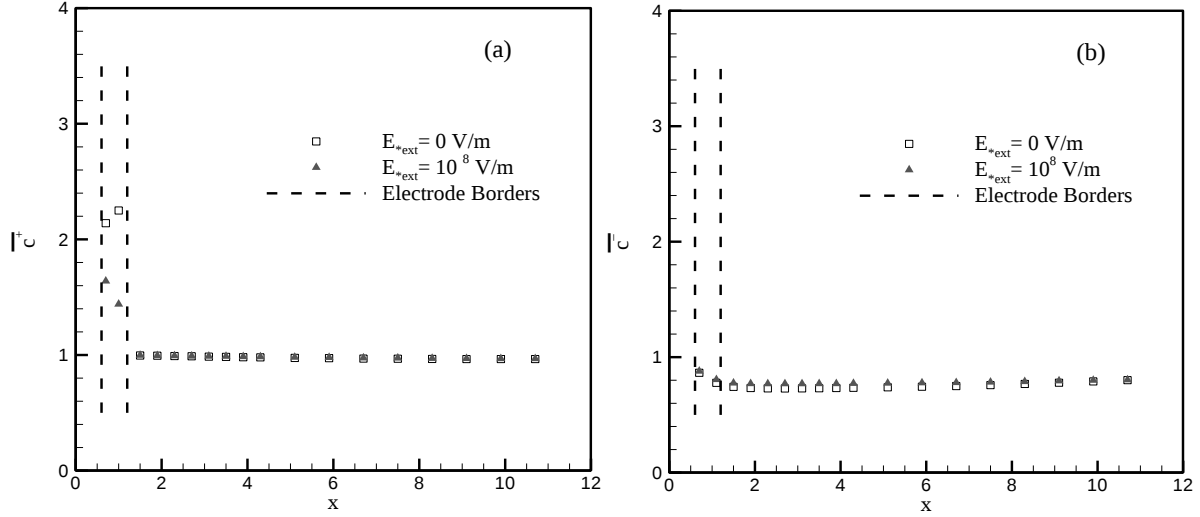


Figure 3.15. Distributions of the average ion concentrations over the lower half of the channel cross-section. (a) Cation concentrations, (b) anion concentrations.

Figure (3.15) depicts that in the lower half of the channel, the averaged cation concentrations are higher than the averaged anion concentrations. Hence, a positive spray current is expected in the lower half of the channel. The net spray current across the entire height is zero at any axial location in the absence of an externally-applied electric field due to the anti-symmetry of the channel. The spray current for the bottom half of the microchannel reads:

$$j_{\text{spray}} = \int_0^1 q u dy \quad (3.51)$$

Figure (3.16) illustrates the dimensionless spray current in the bottom half of the channel for two different values of the longitudinal electric field. In the case with $E_{*ext} = 10^8 \text{ V/m}$, the ion

distribution varies so that the anions in the vicinity of the anode are attracted toward the channel inlet, and cations close to the cathode are drawn away toward the channel outlet. This justifies the slight disparity between the spray current values of the two cases in the middle electrode section.

It is evident from Fig. (3.16) that the longitudinal electric field of $E_{*ext} = 10^8$ V/m has no practical impact on the spray current value along the channel. This implies that the transport of the net charge from the near-electrode polarized layer is performed by viscous scraping rather than the Smoluchowski flow. This could also be the common case in electrostatic atomizers, where the order of the applied longitudinal electric field strength would be similar or lesser than the one applied here. Here, the spray current magnitude in the bottom half reaches a sharp peak value close to the electrode trailing edge and then remains almost constant along the exit section of the channel. This is an indication that at high electrode voltages, diffusion (y-component) does not have a contribution in the exit section of the channel with insulated walls. To achieve an electrified oil at the channel outlet, a separation dielectric plate should be placed at the channel center to segregate the charged liquid in the upper and lower halves with opposite charges from each other.

The current numerical model predicts the liquid charging in the framework of electrokinetic approach^{8,58}, and does not extend to the break-up of the ejected charged liquid from the microchannel atomizer. In any presumed ejection model, the charged liquid should be first considered in the electrokinetic framework until all the charges reach the free surface and making the jet equipotential. In cases where the characteristic hydrodynamic time τ_H is greater than the charge relaxation time τ_C , charges reach the free surface much faster than the free jet evolution. Such cases can be treated in the framework of the Taylor-Melcher leaky dielectric model in the limit explained in Ref. 59. On the other hand, if $\tau_C > \tau_H$ in the free jet, its evolution is fully

describable with the electrokinetic model. The presented results establish the needed boundary conditions for the following free jet problem.

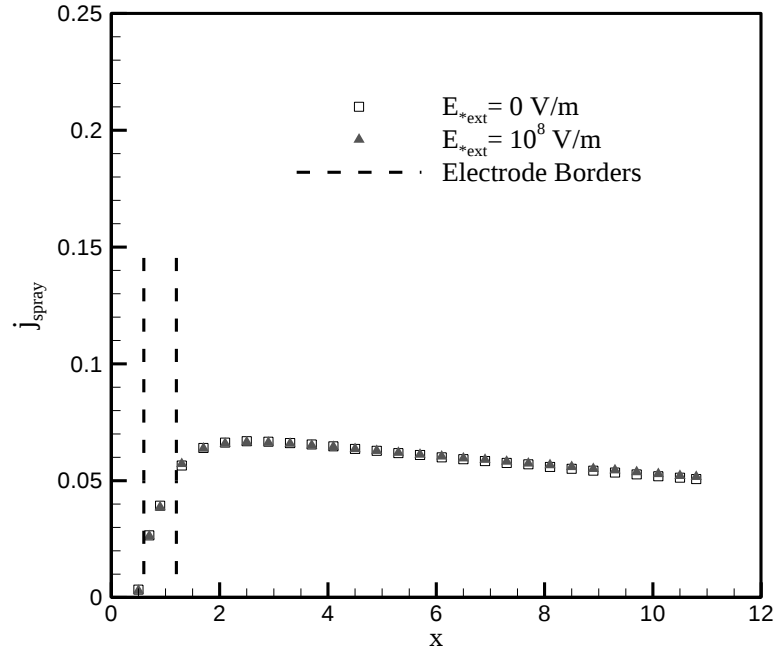


Figure 3.16. Dimensionless spray current magnitude in the bottom half of the channel originating from the cathode.

4. Formation of near electrode layers in ionic conductor liquids at high voltages

(Previously published as Kashir, B., Perri, A., Mashayek, F., and Yarin, A. L. (2019) Theoretical and numerical study of formation of near-electrode layers in ionic conductor liquids at high voltages, *Langmuir* 35, 11080-11088)

4.1. Introduction

The original works of Butler, Volmer, and Frumkin identified the kinetics of near-electrode constituted layers in conducting electrodes^{35,36,39,40}. As a consequence of high electric potential applied at the electrode, crowding of counter-ions happens in ionic conductors such as aqueous solutions, which could potentially increase the thickness of the compact layer⁴⁰. However, this ion crowding is barely feasible in oils, which are the ionic conductor liquids employed in electrostatic atomizers⁴¹. In liquids with very low conductivity, the near-electrode compact layer can only be created through the non-specific adsorption introduced in the work of Stern⁴². The simple one-dimensional compact layer model of Stern⁴², considers it a capacitor with constant capacity C_s . In contrast, the more recent model of Grahame⁴³ differentiates between direct adsorption or with the shell formed by polar molecules, such as aqueous solutions. This hydration is irrelevant in the case of oils. Bazant et al.^{27,28,40} introduced the effective thickness of the Stern compact layer λ_s as a free parameter to account for the potential drop across the compact layer. Stern's or Grahame's model did not consider the cases where electrodes sustain electric current. Nonetheless, the superficial faradaic reactions and the corresponding electric current give rise to oil charging in electrostatic atomizers¹⁵⁻¹⁷.

The idea of a compact layer constituted on a surface exposed to an electrolyte goes back to the classical works of Helmholtz⁴⁴ and Smulochowski⁴⁵. In these cases and the subsequent ones, there was no sustained electric current through the compact layer⁴⁶. The potential drop across the compact layer is of importance in the case of electrostatic atomizers. Due to the low permittivity of canola oil, the majority (almost all the drop) of potential reduction occurs inside the compact layer²⁷. An asymptotic approach was proposed to relate the potential drop across the compact layer to the thickness of this layer⁴⁰. Although the faradaic reactions were considered via appropriate ionic boundary conditions, the compact and diffuse layers were lumped together in the same domain. Moreover, the Stern electric potential boundary condition⁴² was applied for the entire domain.

Here, we propose a novel method to correlate the thickness of the equivalent one-dimensional compact layer to the potential drop occurring across this layer. The kinetics of the governing non-specific adsorption is elaborated, and the thickness is calculated, assuming realistic conditions.

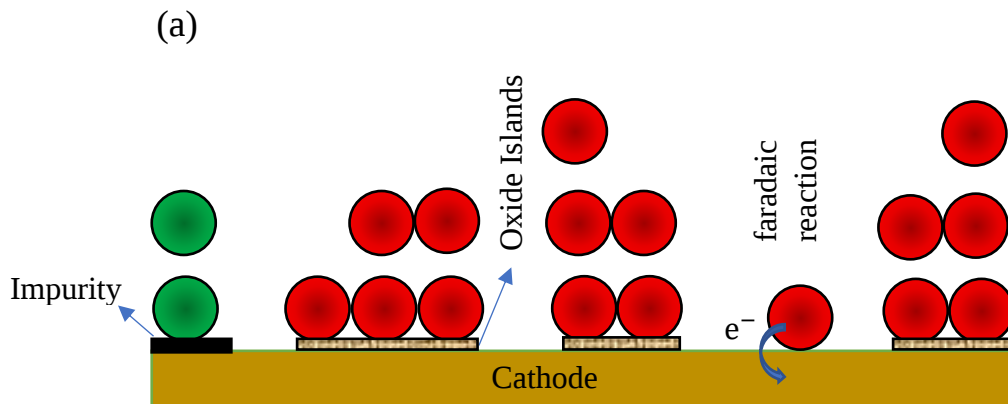
4.2. Non-specific (non-electric) multilayer adsorption

Although the seminal work of Stern was later applied to electrodes with sustained electric current^{26,27}, it is still unclear why some of the counter-ions discharge at the electrode surface, whereas the remaining counter-ions in contact with such an electrode adjoin the compact layer. Stern recognizes the non-specific adsorption/desorption equilibrium of ions at the electrode surface as the primary factor for creating a near-electrode compact layer on a dielectric surface with a non-zero ζ -potential.

Metallic conducting electrodes are covered with oxide islands and/or insulating impurities (to some extent), making it possible to form the compact layers. In this regard, Stern's theory can be generalized to the case of electric-current carrying conducting electrodes, which allows us to relate

the thickness of the equivalent one-dimensional compact layer λ_s to the physical parameters of the occurring electrochemical process rather than using it as a fitting parameter, proposed ad hoc^{26,27}.

Ions can be adsorbed at non-conducting impurities, including oxide islands or stains. Stern⁴² suggested the Langmuir-type⁶⁰ monolayer adsorption, whereas in realistic conditions, non-specific adsorption is also known to create multi-layer patches⁶¹. Hence, we depict a generalized case of the multi-layer adsorption/desorption process following some of the assumptions of the Brunauer-Emmet-Teller (BET) mechanism⁶¹. Suppose that ions (anion or cation) can be adsorbed on top of the oxide islands or stains. Subsequently, ions with similar polarity can create higher layers over the first adsorbed layer. The thickness of the compact layer is considered to be small enough in a way that the ion-ion repulsion or attraction in this layer is negligible compared to the non-electrics attracting ions toward the impurities. However, the ionic electric forces originating from the outer boundary of the compact layer and the forces inside the compact layer can indirectly affect the adsorption process, as explained below. Figure 1 indicates the two and three-dimensional schematics of the compact layer. Ions with distinct polarity are adsorbed non-specifically on surficial impurities.



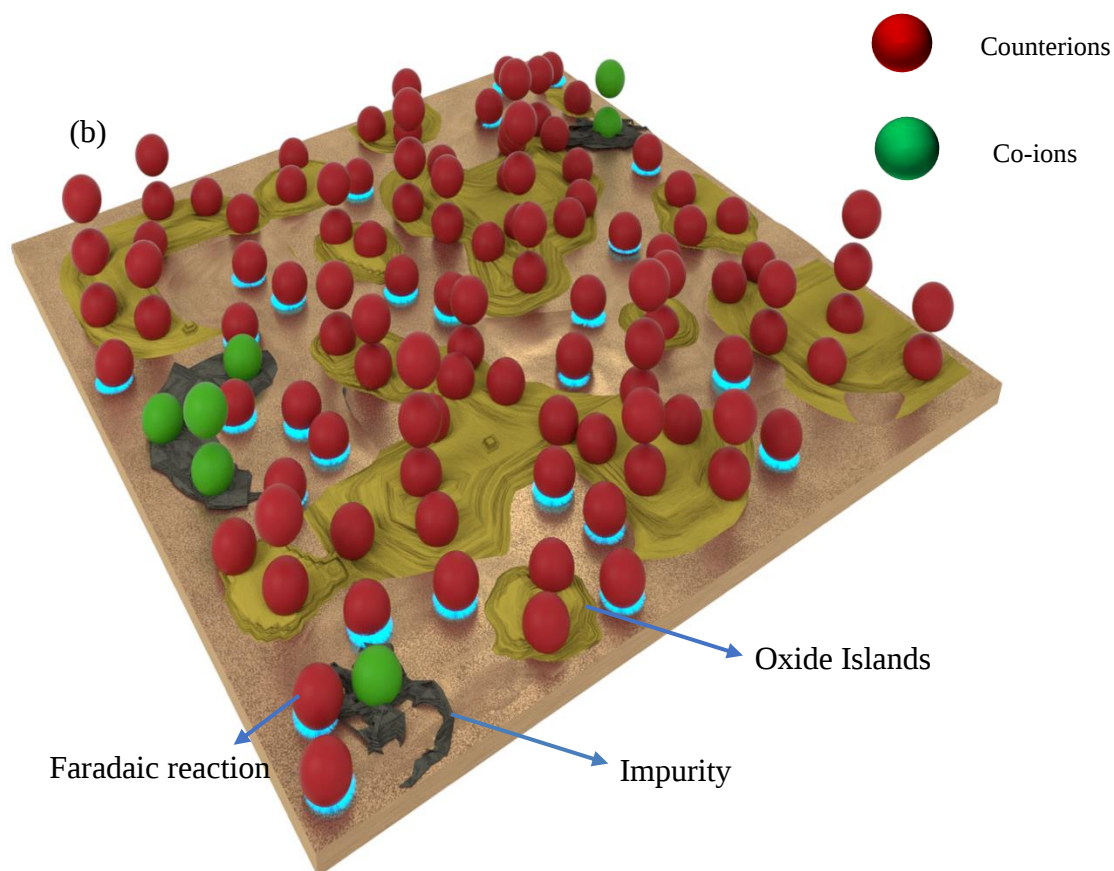


Figure 4.1. Multiple adsorbed ion layers comprising the compact layer. (a) Side view. (b) Isometric view. Red spheres indicate cations, and green ones are anions.

The following clarification is given for the configuration depicted in Fig. (4.1). Based on Earnshaw's theorem, a static system of interacting charges is impossible to exist^{62,63}. However, in the presence of other forces this situation might change. Consider that one ion is already adsorbed in the compact layer through the attractive van der Waals forces between the ion and an oxide island (as in Fig. (4.1)), while another ion with the same polarity is at the distance x from the first ion and away from the electrode surface. The second ion receives an electrostatic repulsive force from the first ion present in the compact layer and an attractive van der Waals force from the electrode surface. The interaction and the resulting balance between the attractive van der Waals

force from the impurities and oxide islands and the Coulombic repulsive force between adsorbed ions can form multi-layers of ions in the compact layer.

The ions present in the first layer of the compact layer are subjected to different forces. An attractive van der Waals force from the surface of the electrode covered with impurities, in addition to a repulsive force from farther ions in the compact layer pushing the first layer toward the impurities on the electrode surface and a repulsive van der Waals force from the underlying impurity molecules constitute these forces. Ions present in the hovering second layer experience an attractive van der Waals force toward the electrode surface and a repulsive Coulombic force from the first layer. The two-layer schematic is depicted in Fig. (4.2).

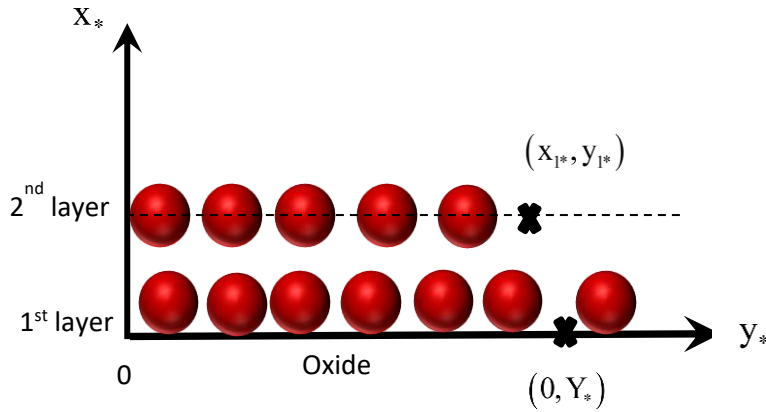


Figure 4.2. Schematic of the two non-specifically adsorbed layers on the oxide islands. Circles indicate ions.

Here we consider the ion charge be equal to the elementary charge e , and the ion densities per unit area in a two-layer configuration are indicated by σ_1 and σ_2 , respectively and possessing the unit of $1/\text{m}^2$. By considering two elements of $dY_* \times 1$ in the first layer and $dy_* \times 1$ in the second

layer, the Coulombic repulsive force reads $f_c = e^2 \sigma_1 \sigma_2 dy_* dY_* / [x_{1*}^2 + (y_{0*} - y_{1*})^2] \times 1^2$. The unit length in the direction perpendicular to the $x_* - y_*$ plane is denoted by $\times 1$. The total Coulombic force applied from the first layer on an element with length dy_* in the second layer is:

$$F_C = e^2 \sigma_1 \sigma_2 dy_* \int_{-\infty}^{+\infty} \frac{dY_*}{[(y_{0*} - y_{1*})^2 + x_{1*}^2]} = \frac{\pi e^2 \sigma_1 \sigma_2 dy_*}{x_{1*}} \quad (4.1)$$

Here and hereinafter, the multipliers $\times 1^2$ with the units of $1/m^2$ are neglected for brevity. The Lennard-Jones potential⁶⁴ reads:

$$W(r_*) = -\frac{C_1}{r_*^6} + \frac{C_2}{r_*^{12}} \quad (4.2)$$

where W marks the Lennard-Jones potential, $C_1 = 10^{-27} \text{ Jm}^6$ and $C_2 = 10^{-134} \text{ Jm}^{12}$ are the coefficients of the attractive and repulsive parts, respectively⁶⁴, and $r_* = \sqrt{x_{1*}^2 + (y_{0*} - y_{1*})^2}$ identifies the distance between interacting ingredients.

The van der Waals force as the derivative of the Lennard-Jones potential is found as:

$$f_w(r_*) = -\frac{dW}{dr_*} = -\frac{6C_1}{r_*^7} + \frac{12C_2}{r_*^{13}} \quad (4.3)$$

In the second layer, the repulsive component of the van Waals force becomes negligible, i.e.

$f_w(r_*) = -\frac{6C_1}{r_*^7}$. Therefore, the van der Waals attractive force between elements with areas $dY_* \times 1$ and $dy_* \times 1$ in the first and second layers, yields⁶⁵:

$$F_W(r_*) = -6C_1 \sigma_1 \sigma_2 dy_* \int_{-\infty}^{+\infty} \frac{dY_*}{[(y_{0*} - y_{1*})^2 + x_{1*}^2]^{7/2}} = -\frac{32}{5} C_1 \sigma_1 \sigma_2 \frac{dy_*}{x_{1*}^6} \quad (4.4)$$

The multipliers $\times 1^2$ with the units $1/m^2$ are disregarded for shortness.

The Hamaker constant A is defined as⁶⁴:

$$A = \pi^2 C_1 \rho_1 \rho_2 \quad (4.5)$$

Here, ρ_1 and ρ_2 are the volumetric number density of interacting bodies (ions or molecules) in the layers with the units $1/\text{m}^3$. The volumetric number density and surface area density in each layer are related as

$$\frac{\sigma_i}{d} = \rho_i \quad (i = 1, 2) \quad (4.6)$$

where d is the characteristic diameter of interacting bodies i.e. ions.

Replacing Eq. (4.6) into (4.5) gives

$$A = \pi^2 C_1 \frac{\sigma_1 \sigma_2}{d^2} \quad (4.7)$$

Finally, we rewrite Eq. (4.4) as

$$F_w(r_*) = -\frac{32}{5\pi^2} A d^2 \frac{dy_*}{x_{1*}^6} \quad (4.8)$$

The balance of forces for an element with length dy_* in the second layer of the compact layer becomes:

$$\frac{\pi e^2 \sigma_1 \sigma_2 dy_*}{x_{1*}} = -\frac{32}{5\pi^2} A d^2 \frac{dy_*}{x_{1*}^6} \quad (4.9)$$

Simplifying relation (4.9) yields the distance between the second layer and the first layer attached to the impurities as:

$$x_{1*} = \left[\frac{32}{5\pi^3} \frac{A d^2}{e^2 \sigma_1 \sigma_2} \right]^{1/5} \quad (4.10)$$

Based on available data in Ref. 64, the thickness of a two-layer configuration with the ion diameter $d=0.4$ nm and the volumetric number densities $\rho_1 = \rho_2 = 3 \times 10^{28} \text{ 1/m}^3$ becomes 15 nm. The Hamaker constant is 10^{-19} J, and the elementary charge is 1.6×10^{-19} C. The calculated value of 15 nm is in the expected order of the Stern layer thickness⁴⁰. It should be mentioned that

systems with additional layers can be created following the same logic in the balance of interacting forces, including the Coulombic and van der Waals forces.

Figure (4.3) demonstrates a three-layer configuration for the compact layer in conjunction with the diffuse layer ions, which are at the average distance of the Debye length λ_D from the surface of the electrode.

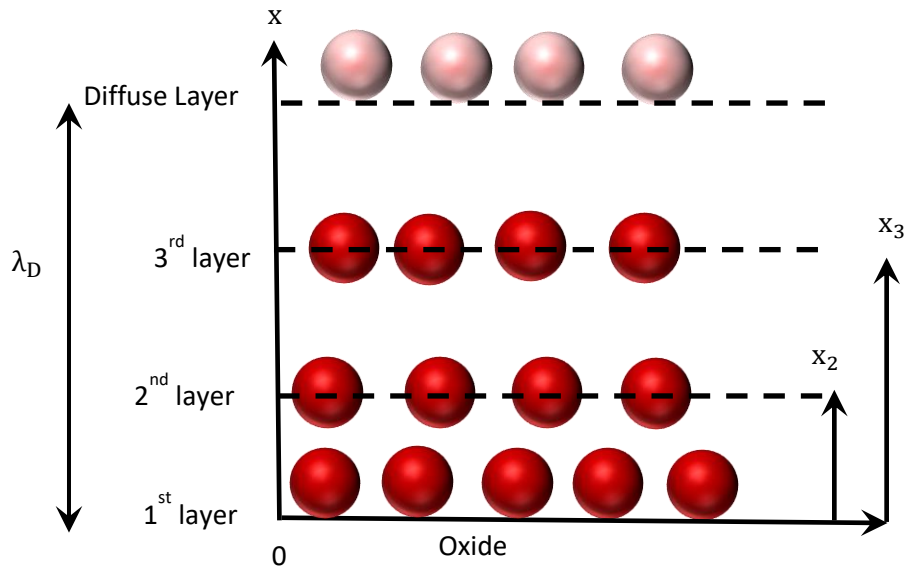


Figure 4.3. Schematic of the three non-specifically adsorbed layers (red color) on an oxide island along with the ions (pastel color) present in the hovering diffuse layer.

The dimensionless balance equations for a system of two hovering layers in a three-layer structure (cf. Figure (4.3)) reads

$$j = 2: \frac{\bar{\rho}_2 \bar{\rho}_1}{\bar{x}_2} - \frac{\bar{\rho}_2 \bar{\rho}_3}{\bar{x}_3 - \bar{x}_2} - \frac{\bar{\rho}_2 \bar{\rho}_{d.l.}}{\bar{\lambda}_D - \bar{x}_2} - \frac{\bar{\rho}_1 \bar{\rho}_2}{\bar{x}_2^6} = 0 \quad (4.11)$$

$$j = 3: \frac{\bar{\rho}_3 \bar{\rho}_1}{\bar{x}_3} - \frac{\bar{\rho}_2 \bar{\rho}_3}{\bar{x}_3 - \bar{x}_2} - \frac{\bar{\rho}_3 \bar{\rho}_{d.l.}}{\bar{\lambda}_D - \bar{x}_3} - \frac{\bar{\rho}_1 \bar{\rho}_3}{\bar{x}_3^6} = 0 \quad (4.12)$$

Here, $\bar{x}_2$ and $\bar{x}_3$ are the dimensionless distance of the second and third hovering layers from the first layer attached to the oxide islands and $\bar{\lambda}_D$ marks the dimensionless Debye length. The scale is x_{1*} from Eq. (4.10). The dimensionless volumetric number densities of the layers are $\bar{\rho}_1$, $\bar{\rho}_2$ and $\bar{\rho}_3$. The third term on the left-hand side of Eqs. (4.11) and (4.12) indicates the repulsive force from the diffuse layer acting on the second and third layers of the compact layer ($j=2$ and 3). The volumetric number density related to atoms (ions) of the radius 0.2 nm ($\rho_* = 3 \times 10^{28} \text{ 1/m}^3$) is used as the scale. $\bar{\rho}_{d.l.}$ indicates the volumetric number density in the diffuse layer.

The inherent ζ -potential of the oxide islands is thoroughly screened by combining the compact and diffuse layers. If we present the dimensionless volumetric number density in the oxide islands as $\bar{\rho}_0$, the full screening condition becomes:

$$\bar{\rho}_{d.l.} = \bar{\rho}_0 - (\bar{\rho}_1 + \bar{\rho}_2 + \bar{\rho}_3) \quad (4.13)$$

By taking $\bar{\rho}_0 = 1.5$ and $\bar{\rho}_1 = 1$ as constant parameters and increasing the value of $\bar{\rho}_2$, the parameters $\bar{\rho}_3$ and $\bar{\rho}_{d.l.}$ can be found from relation (4.13) interdependently. By specifying the volumetric number densities, the system of Eqs. (4.11) and (4.12) can be solved numerically to find the physically acceptable (order of layers) solutions. In the case of canola oil, the Debye length is $\lambda_D = 3.1 \text{ }\mu\text{m}$. Based on x_{1*} as the length scale, $\bar{\lambda}_D = 210$. Table (4.1) represents the physical solutions for the second and third layers. By increasing $\bar{\rho}_3$ (the dimensionless volumetric number density in the third layer), the position of this layer moves away from the oxide island surface. The second hovering layer (i.e., third layer in the compact layer) is two orders of magnitude farther from the first hovering layer (i.e., the second layer in the compact layer). The second hovering layer experiences repulsive Coulombic force from the first hovering layer and the layer attached to the oxide islands. In contrast, the first hovering layer is repelled electrostatically from the

electrode surface only by the layer attached to the oxide islands. Remarkably, the distance between the second hovering layer (third layer in the compact layer) and the electrode surface is much less than the Debye length. Hence, diffusion in the flow field can not influence the second hovering layer. Moreover, convection in the bulk flow can only play a role in affecting the second hovering layer when the longitudinal velocity component be in the order of 10^{-4} cm/s or higher, which comes from the comparison of Coulomb and Stokes forces acting on a hovering ion.

Table 4.1. Distances of the hovering layers of the compact layer from the oxide layer surface

$\bar{\rho}_1$	$\bar{\rho}_2$	$\bar{\rho}_3$	$\bar{\rho}_{d,l}$	$\bar{x}_2$	$\bar{x}_3$
1	10^{-10}	5×10^{-20}	0.4999999999	1.0	140.0
1	10^{-4}	10^{-5}	0.49989	1.0	140.0
1	10^{-4}	5×10^{-5}	0.49985	1.0	140.0
1	10^{-3}	10^{-5}	0.49899	1.0	140.1
1	10^{-3}	5×10^{-5}	0.49895	1.0	140.1
1	10^{-2}	10^{-3}	0.489	1.0	141.5
1	10^{-2}	5×10^{-3}	0.485	1.0	141.9
1	5×10^{-2}	10^{-3}	0.449	1.0	147.1
1	5×10^{-2}	5×10^{-3}	0.445	1.0	147.5

Let us indicate the fraction of the non-conducting islands on the electrode with no ion adsorption as θ_0 . Also, denote the kinetic constant of the adsorption process on the i -th layer as $k_{f,i}$ and denote the kinetic coefficient of the desorption process from the i -th layer as $k_{b,i}$. For brevity, the kinetic coefficients are considered the same in the adsorption/desorption processes for anions and cations. Adsorption of a single ion immediately on the oxide islands will transfer an

empty site to a part of the first layer. The kinetic equation for the ion-free sites in the non-conducting oxide islands or impurities at the electrode surface reads

$$\frac{d\theta_0}{dt_*} = k_{b,1}\theta_1^\pm - k_{f,1}c_*^\pm\theta_0 \quad (4.14)$$

Here, $\theta_1^\pm$ indicate the fraction of the non-conducting islands covered with a layer of ions. The first term on the right-hand side of Eq. (4.14) denotes the desorption from the first layer, which adds to the ion-free sites on the non-conducting oxide islands or the impurities at the electrode surface. The second term on the right-hand side indicates ion adsorption on non-conducting islands that adds to the fraction of ion-covered parts in these islands.

The kinetic equation for the i -th layer in a multilayer structure of the compact layer becomes

$$\frac{d\theta_i^\pm}{dt_*} = -k_{b,i}\theta_i^\pm + k_{f,i}c_*^\pm\theta_{i-1}^\pm + k_{b,i+1}\theta_{i+1}^\pm - k_{f,i+1}c_*^\pm\theta_i^\pm \quad (4.15)$$

where $\theta_i^\pm$ denotes the parts of the non-conducting islands with i layers of ions atop.

The first and third terms on the right-hand side of Eq. (4.15) indicate desorption from the i -th and $(i+1)$ -th layers, respectively. On the other hand, the second and fourth terms demonstrate the adsorption process from the outer boundary of the compact layer onto the $(i-1)$ -th and i -th layers, respectively.

In equilibrium, time derivatives become zero, and the following system of equations is obtained for $(i-1)$ layers constituted atop the non-conducting islands:

$$k_{b,1}\theta_1^\pm - k_{f,1}c_*^\pm\theta_0 = 0 \quad (4.16)$$

$$-k_{b,1}\theta_1^\pm + k_{f,1}c_*^\pm\theta_0 + k_{b,2}\theta_2^\pm - k_{f,2}c_*^\pm\theta_1^\pm = 0 \quad (4.17)$$

$$-k_{b,i-1}\theta_{i-1}^{\pm} + k_{f,i-1}c_{*}^{\pm}\theta_{i-2}^{\pm} + k_{b,i}\theta_i^{\pm} - k_{f,i}c_{*}^{\pm}\theta_{i-1}^{\pm} = 0 \quad (4.18)$$

By replacing Eq. (4.16) into Eq. (4.17) and so on, the following system of equations is obtained

$$k_{b,2}\theta_2^{\pm} - k_{f,2}c_{*}^{\pm}\theta_1^{\pm} = 0 \quad (4.19)$$

$$k_{b,i}\theta_i^{\pm} - k_{f,i}c_{*}^{\pm}\theta_{i-1}^{\pm} = 0 \quad (4.20)$$

It is plausible to assume that ion adsorption/desorption on any occupied layer possesses identical kinetic characteristics, that is, $k_{f,i} = k_{f,2}$ and $k_{b,i} = k_{b,2}$ for $i > 2$, whereas the adsorption/desorption on the empty surface itself is different, that is, the kinetic coefficients $k_{f,1} \neq k_{f,2}$ and $k_{b,1} \neq k_{b,2}$. Hence, the solutions of Eqs. (4.19) - (4.20) read

$$\theta_1^{\pm} = Y^{\pm}\theta_0 \quad (4.21)$$

$$\theta_2^{\pm} = X^{\pm}\theta_1^{\pm} = Y^{\pm}X^{\pm}\theta_0 = K(X^{\pm})^2\theta_0 \quad (4.22)$$

$$\theta_i^{\pm} = K(X^{\pm})^i\theta_0 \quad (4.23)$$

with

$$Y^{\pm} = \frac{k_{f,1}c_{*}^{\pm}}{k_{b,1}}, \quad X^{\pm} = \frac{k_{f,2}c_{*}^{\pm}}{k_{b,2}}, \quad K = \frac{Y^{\pm}}{X^{\pm}} \quad (4.24)$$

By considering the number of constituted layers (i) and the fraction of non-conducting islands covered by ions in each layer (θ_i), the equilibrium number of ions present in the unit surface area of the compact layer reads

$$n_{eq}^{\pm} = \sum_{i=1}^{\infty} i\theta_i^{\pm} = K\theta_0 \sum_{i=1}^{\infty} i(X^{\pm})^i = K\theta_0 \frac{X^{\pm}}{(1-X^{\pm})^2} \quad (4.25)$$

The summation to infinity is initially introduced in the Baunauer-Emmet-Teller (BET) mechanism⁶¹, which can be a realistic limit when the ion size is negligible compared to the unit surface area of non-conducting islands.

Adding fractions of non-conducting islands covered with anions and cations and the empty fraction together yields

$$\sum_{i=1}^{\infty} \theta_i^+ + \sum_{i=1}^{\infty} \theta_i^- + \theta_0 = 1 \quad (4.26)$$

Replacing Eq. (4.23) into (4.26) gives

$$K\theta_0 \sum_{i=1}^{\infty} (X^+)^i + K\theta_0 \sum_{i=1}^{\infty} (X^-)^i + \theta_0 = 1 \quad (4.27)$$

For the summation of geometric progressions in Eq. (4.27) we have

$$\sum_{i=1}^{\infty} (X^+)^i = \frac{X^+}{1-X^+}, \sum_{i=1}^{\infty} (X^-)^i = \frac{X^-}{1-X^-} \quad (4.28)$$

Solving for θ_0 based on Eqs. (4.27) and (4.28) gives

$$\theta_0 = \frac{1}{1+K[X^+/(1-X^+)+X^-/(1-X^-)]} \quad (4.29)$$

Substituting θ_0 in Eq. (4.25) provides the equilibrium dimensionless charge density as

$$n_{eq}^{\pm} = K \frac{X^{\pm}}{(1-X^{\pm})^2 \{1+K[X^+/(1-X^+)+X^-/(1-X^-)]\}} \quad (4.30)$$

Based on Eq. (4.24), we have $Y^{\pm} = KX^{\pm}$. Rearranging Eq. (4.30) yields

$$n_{eq}^{\pm} = \frac{Y^{\pm}}{(1-X^{\pm})^2 [1+Y^+/(1-X^+)+Y^-/(1-X^-)]} \quad (4.31)$$

Defining two dimensionless parameters for the system as

$$\alpha = \frac{k_{f,1}c_{*\infty}}{k_{b,1}}, \beta = \frac{k_{f,2}c_{*\infty}}{k_{b,2}} \quad (4.32)$$

Substituting introduced parameters in Eq. (4.31) yields the final form as

Then, Eq. (4.31) takes the form

$$n_{eq}^{\pm} = \frac{Y^{\pm}}{(1-\beta c^{\pm})^2 [1+Y^+/(1-\beta c^+)+Y^-/(1-\beta c^-)]} \quad (4.33)$$

with $c^{\pm}$ being the dimensionless cation and anion concentrations at the outer boundary of the compact layer (at the interface with the diffuse layer).

In the case when polarization at the outer boundary of the compact layer due to the electric field is insignificant, i.e. $c^+ \approx c^-$, and a monolayer adsorption (i.e., $\beta = 0$), one obtains from Eq. (4.33) the following relation:

$$(n_{eq}^{\pm})_{\text{Langmuir-Stern}} = \frac{Y^{\pm}}{[1+Y^++Y^-]} = \frac{k_{f,1}c_{*}^{\pm}/k_{b,1}}{1+k_{f,1}c_{*}^+/k_{b,1}+k_{f,1}c_{*}^-/k_{b,1}} = \frac{\alpha c^{\pm}}{1+\alpha c^++\alpha c^-} = \frac{\alpha c^{\pm}}{1+2\alpha c^{\pm}} \quad (4.34)$$

Equation (4.34) corresponds to the Langmuir adsorption isotherm⁶⁰ in the heteropolar adsorption case considered by Stern⁴² under such conditions. Note that in the case of an insignificant polarization at the outer surface of the compact layer, i.e., $c^+ \approx c^-$, and thus $X^+ = X^- = X$, Eq. (4.33) yields

$$n_{eq}^{\pm} = \frac{\alpha c^{\pm}}{(1-X)[1+2\alpha c^{\pm}-X]} > (n_{eq}^{\pm})_{\text{Langmuir-Stern}} \quad (4.35)$$

A single-ion-occupied site has the area⁶⁶ $A_0 = 16.2 \text{ }^\circ\text{A}^2$. Then, the magnitude of charges in the compact layers on the cathode and anode are, respectively,

$$|Q_{\text{cathode}}| = e(n_{\text{eq}}^+ - n_{\text{eq}}^-), \quad |Q_{\text{anode}}| = e(n_{\text{eq}}^- - n_{\text{eq}}^+) \quad (4.36)$$

Following Stern⁴² and considering the equivalent one-dimensional compact layers on the cathode and anode as plane capacitors and employing Eq. (4.36) one obtains for the cathode

$$\frac{\varepsilon\varepsilon_0 S}{\lambda_S} |-V_{0*} + \psi_1| = \frac{eS}{A_0} (n_{\text{eq}}^+ - n_{\text{eq}}^-) \quad (4.37)$$

and for the anode

$$\frac{\varepsilon\varepsilon_0 S}{\lambda_S} (V_{0*} - \psi_1) = \frac{eS}{A_0} (n_{\text{eq}}^- - n_{\text{eq}}^+) \quad (4.38)$$

In Eqs. (4.37) and (4.38) $-V_{0*}$ ($V_{0*} > 0$) is the cathode potential, and V_{0*} is the anode potential, whereas $\mp\psi_1$ (with $\psi_1 > 0$) are the corresponding potentials at the outer boundary of the compact layers, where the electron transfer corresponding to faradaic reactions happens. S is the electrode surface area (the SI units are used).

Note that the consideration of the two-dimensional island pattern shown in Fig. (4.1)(b) as a one-dimensional one shown in Fig. (4.1)(a), which stems from the original Stern model⁴² and is used here, is essentially the mean-field approximation; its validity is discussed in section (4.4).

It should be emphasized that the compact layer capacitance C_S is, according to Eq. (4.38),

$$C_S = \frac{\varepsilon\varepsilon_0 S}{\lambda_S} \quad (4.39)$$

Equations (4.37) and (4.38) are identical in this case, and thus the thickness of the equivalent one-dimensional compact layer λ_S is found as

$$\lambda_S = \frac{\varepsilon\varepsilon_0 A_0}{e(n_{\text{eq}}^- - n_{\text{eq}}^+)} (V_{0*} - \psi_1) \quad (4.40)$$

which relates λ_S to ψ_1 and, through Eq. (4.33), to the other physical parameters of the electrochemical process.

According to Eq. (4.35), one should expect that multilayer ion adsorption makes the equivalent one-dimensional Stern layer thinner because a higher charge can be accumulated at the compact-layer ‘capacitor’ at a fixed potential difference, i.e., its capacitance increases.

4.3. Electro-kinetic problem in the diffuse layer

The Open Field Operation and Manipulation (OpenFOAM) toolbox⁵³ is employed to solve the electro-kinetic problem in the diffuse layer above the compact layer to predict concentrations of the cations and anions $c_*^\pm$ required to predict $n_{eq}^\pm$ according to Eq. (4.35). The following set of equations is solved numerically:

$$\frac{\partial c_*^+}{\partial t_*} = D \nabla^2 c_*^+ + \frac{De}{k_B T} \nabla \cdot (c_*^+ \nabla \varphi_*) \quad (4.41)$$

$$\frac{\partial c_*^-}{\partial t_*} = D \nabla^2 c_*^- - \frac{De}{k_B T} \nabla \cdot (c_*^- \nabla \varphi_*) \quad (4.42)$$

$$\nabla^2 \varphi_* = - \frac{q_*}{\epsilon \epsilon_0} \quad (4.43)$$

A one-dimensional anodic half-cell is considered to investigate the thicknesses of the compact and diffuse layers. The ionic concentrations and electric potential distribution inside the diffuse layer are found numerically by solving Eqs. (4.41) - (4.43) to predict concentrations $c_*^\pm|_{\text{interface}}$ at the interface between the diffuse and the compact layers. Then, these concentrations are used to predict the equilibrium dimensionless charge densities $n_{eq}^\pm$ in the equivalent one-dimensional layer.

The one-dimensional half-cell case is considered, in which an anode is in contact with an electrolyte at rest (cf. Figure (4.4)). The computational domain begins from the bulk and ends at the interface. The overall length scale is $H_* = 10 \text{ } \mu\text{m}$. The bulk ion concentration is taken as $c_{*\infty} = 8 \times 10^{17} \text{ 1/m}^3$, and $y_* = 0$ indicates the electroneutral bulk boundary.

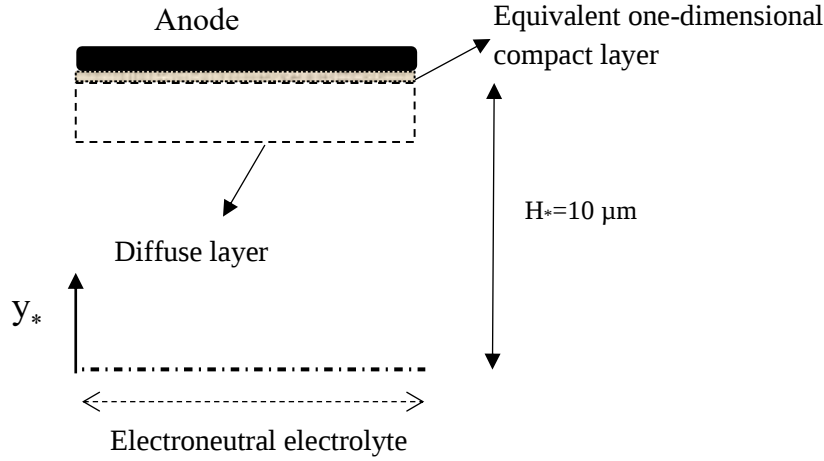


Figure 4.4. The anodic half-cell.

The electric current density at the interface is found using the Frumkin-Butler-Volmer kinetics with the parameters based on the experiments¹⁷. The electric current density for the anodic oxidation process in the Tafel form (including the Frumkin correction) is as follows¹⁷

$$J_{e*} = 10^{\{[V_{0*}/2 - (a_a + \psi_1)]/b_a\}} \left[\frac{\text{A}}{\text{cm}^2} \right] \quad (4.44)$$

where $V_{0*}/2$ is the voltage at the anode, $a_a + \psi_1$ and b_a are the experimentally measured coefficients equal to $0.99996(V_{0*}/2) + 1.05123$ and 0.1118 , respectively. The cations flux $j_*^+ = 0$ at the anode, whereas $j_*^- > 0$. The boundary conditions for the anions and cations at the anode surface are given in relations (3.47) - (3.48).

The boundary conditions in the bulk read $c_*^\pm = c_{*\infty}$. The electric potential in the bulk is chosen as $\varphi_* = 0$ V, while the value at the interface is $\varphi_* = \psi_1 = 10$ V. The anode voltage is taken as $V_{0*}/2 = 1750$ V.

In the simulation, the finest cell at the interface was 0.63 nm. The results are rendered dimensionless with the following scales: H_* for y_* , $c_{*\infty}$ for c_*^+ and c_*^- , and $ec_{*\infty}$ for q_* . The predicted dimensionless ion concentrations at the interface were $c^+|_{\text{interface}} = 0$, $c^-|_{\text{interface}} = 37500$. The predicted dimensionless ion and charge density distributions across the half-cell are shown in Fig. (4.5). The thickness of the diffuse layer λ_d is found to be 90 nm.

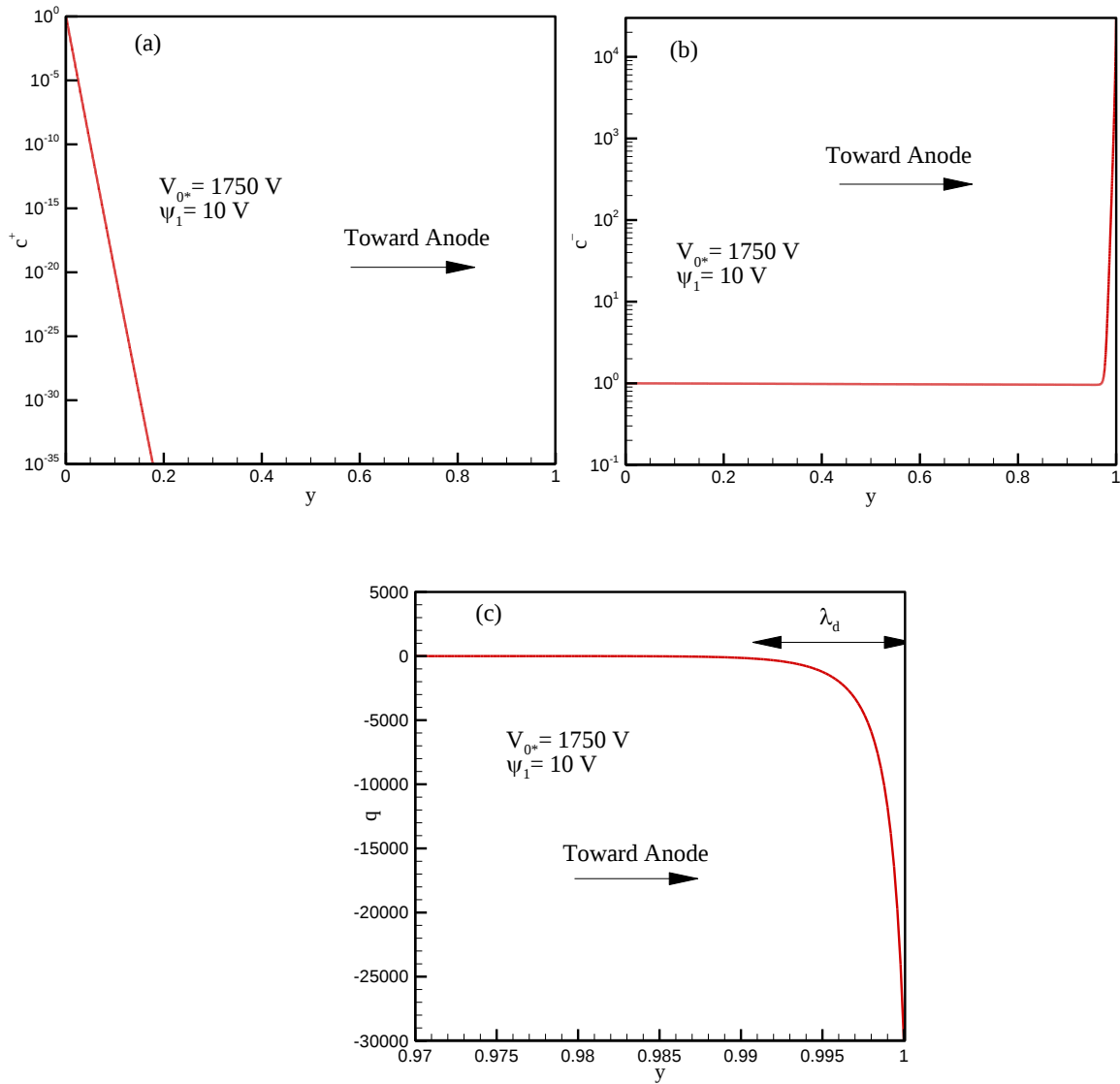


Figure 4.5. Dimensionless distributions across the anodic half-cell: (a) cation concentration, (b) anion concentration, (c) net charge density.

Then, the thickness of the equivalent one-dimensional compact layer λ_s and the capacitance of the compact layer are found for several values of the adsorption kinetic parameters α and β . The lesser values of β compared to α are employed because it is expected that a higher ratio of the adsorption to desorption rate is at the bare electrode surface than on the ionic layers. The results are listed in Table (4.2). It is seen that the value of α practically does not affect the thickness of the equivalent one-dimensional compact layer and thus its capacitance. At $\beta=0$, only monolayer adsorption is possible (only the Langmuir adsorption). As the value of β increases, multi-layer adsorption patches become possible, the thickness of the equivalent one-dimensional compact layer λ_s decreases, whereas the capacitance increases. At a certain limiting value of β , $\lambda_s = 0$ and thus the infinite capacitance $C_s = \infty$ is reached. Therefore, there exists a limiting value of the second adsorption-to-desorption ratio β beyond which the model of the equivalent one-dimensional compact layer cannot be used.

Table 4.2. Thickness and capacitance of the equivalent compact layer for several values of the kinetic parameters α and β . The capacitance is calculated for the electrode area of $S= 1 \text{ cm}^2$.

α	β	n_{eq}^-	$\lambda_s \text{ (nm)}$	$C_s \text{ (}\mu\text{F)}$	α	β	n_{eq}^-	$\lambda_s \text{ (nm)}$	$C_s \text{ (}\mu\text{F)}$
1	0	1.0	40.0	0.07	10	0	1.0	40.0	0.07
1	0.00001	1.6	25.0	0.11	10	0.00001	1.6	25.0	0.11
1	0.00002	4.0	10.0	0.27	10	0.00002	4.0	10.0	0.27
1	0.000022	5.7	7.0	0.38	10	0.000022	5.7	7.0	0.38

1	0.000024	10.0	4.0	0.66	10	0.000024	10.0	4.0	0.66
1	0.000026	40.0	1.0	2.66	10	0.000026	40.0	1.0	2.66

Using the data from electron microscopy, it was found that in the case of Cu, the oxide island diameter is 65 Å, and the interisland spacing is 40 Å, i.e., 6.5 nm and 4 nm, respectively⁶⁷. Similarly, for Ni, the oxide island diameter is 2.5-3 nm, and interisland spacing is 2 nm, and for Ti the oxide island diameter is 1.5-2 nm, and the interisland spacing is below the resolution threshold (below ~1 nm). The predicted thickness of the compact layer λ_s listed in Table (4.1) is either much larger than the oxide island diameter and the interisland spacing or comparable to them. This comparison shows that the mean-field approximation involved in the treatment of the two-dimensional island pattern of Fig. (4.1)b as a one-dimensional one of Fig. 1a, which is embedded in the original Stern layer model⁴² (the case of $\beta=0$), and implemented here (the cases $\beta \geq 0$), is approximately valid: better for Ti than for Ni, and then Cu.

4.4. Validity of one-dimensional compact layer

The Stern layer thickness can be measured, for example, by X-ray photoelectron spectroscopy (XPS)⁶⁸. The results are intriguing because the measurements reveal that ‘the Stern layer compresses (becomes thinner) as the electrolyte concentration is increased’. This counter-intuitive result is in line with the predictions of the present theory that multilayer ion adsorption makes the equivalent one-dimensional Stern layer thinner because of the accumulation of a higher charge at the compact-layer ‘capacitor’ at a fixed potential difference, i.e., an increase in the Stern layer

capacitance. In more concentrated electrolytes⁶⁸ multilayer ion adsorption is facilitated, and accordingly, the Stern layer becomes thinner.

Applications such as electrostatic atomizers used for charging oils, kerosene, and diesel fuel to facilitate their secondary atomization and finer dispersion and multiple electrohydrodynamic devices transporting the so-called dielectric liquids can benefit significantly from the insight into the nature of the near-electrode compact layer achieved in this work. It is shown that, at high voltages, the major potential drop occurs at the compact layer²⁷, and the boundary conditions in any theoretical and numerical simulations could be imposed at the interface of the compact and diffuse layers⁴¹. It should be emphasized that liquid charging by means of the so-called charge emission at the tip of a needle electrode in electrospinning, electrospraying, and electrostatic atomization proceeds due to faradaic reactions responsible for the formation of a nearby polarized layer in the ionic conductor liquid, which is issued as a flowing charged liquid jet^{14,16,17,63,69,70}. It is highly effective due to the high electric field strength near the tip of the electrode; however, it has the same physical nature as in the near plane electrode zone in model microchannel atomizers⁴¹. The latter case is described by an easier theoretical/ numerical description, which is the main reason that it has been studied in detail. In contrast, the needle electrodes are more involved, and their numerical investigations are still underway. Note also that because the thickness of the Stern layer is much smaller than any practically possible radius of curvature of the needle electrode tip, the planar theory of the Stern layer holds without any restrictions.

5. Slow discharge theory and calculation of the potential drop across the compact layer

(Previously published as Kashir, B., Perri, A., Yarin, A. L., and Mashayek, F. (2019) Slow discharge theory and calculation of the potential drop across the compact layer at high electrode voltages. *Langmuir* 35, 14458-14464)

5.1. Introduction

The computational models proposed for electrokinetic and electrohydrodynamic flows are based on the ionic transport equations and account for the flux of counter-ions at the electrode surface due to faradaic reactions. These equations are solved starting from the interface of the compact and diffuse layers^{27,28}. Accordingly, in such models, the value of the electric potential at the interface is required as a boundary condition. In ionic conductor liquids with low dielectric constant and significant potential drop across the compact layer, calculating the value of the electric potential at the interface of the compact and diffuse layers is desirable, rather than imposing an ad hoc value as in the previous studies^{27,28}. Specifically, both the thickness and potential drop across the compact layer were unknown parameters in these studies and inevitably one should be estimated to calculate the second parameter thereof. Here, we propose an approach which stems from the Frumkin slow discharge theory and allows one to calculate the potential drop across the compact layer directly, rather than using it as a parameter assumed ad hoc.

The Frumkin slow-discharge theory describes the kinetics of heterogeneous charge transfer reactions and considers the electrostatic interaction of reactants and products with a charged interface⁴⁷. The theory can be re-formulated in the framework of the quantum-chemical approach of the Marcus theory⁴⁸. Electron transfer through faradaic reactions at the electrode surface in

electrostatic atomization is kinetics-limited (slow), rather than diffusion-limited (fast)¹⁶. The microscopic electron transfer theory, proposed by Marcus⁴⁹, predicts reaction rates for heterogeneous electrode reactions⁷². The fundamental feature of the Marcus theory is the quadratic dependence of the reactant and product free energy on a configurational reaction coordinate, where electron transfer occurs iso-energetically at the intersection of potential energy parabolas.

Here, we employ the formulation of the Frumkin slow discharge theory to calculate the electric potential at the interface of the compact and diffuse layers in the context of the ionic conductor liquids. The activation energy present in the Frumkin formulation is calculated from the Marcus electron transfer theory. The heterogeneous electron transfer energy is discussed in section 5.2. In contrast, section 5.3 presents the governing equations of the computational model and the proposed numerical approach to predict and correct the interface voltage by employing the Frumkin slow discharge theory. Results and discussions for two examples for the canola oil as the ionic conductor liquid in electrostatic atomization are provided in section 5.4.

5.2. Heterogeneous electron transfer energy

For electrodes' redox (reduction or oxidation, $\text{Ox} + e \rightleftharpoons \text{Red}$) reactions, Marcus⁷³ suggested the following expressions for the electron transfer activation energy based on the energy level parabolas:

$$\Delta G_* = N_A \left(\frac{\lambda_{el}}{4} \left[1 + \frac{e\eta_*}{\lambda_{el}} \right]^2 \right) \left[\frac{\text{J}}{\text{mol}} \right] \quad \text{Reduction process} \quad (5.1)$$

$$\Delta G_* = N_A \left(\frac{\lambda_{el}}{4} \left[1 - \frac{e\eta_*}{\lambda_{el}} \right]^2 \right) \left[\frac{\text{J}}{\text{mol}} \right] \quad \text{Oxidation process} \quad (5.2)$$

where ΔG_* is the activation energy for the electron transfer, η_* is the over-potential, and λ_{el} is the reorganization energy.

The over-potential in Eqs. (5.1) and (5.2) is defined as the difference of the electrode potential from the formal potential and is expressed as⁷⁴:

$$\eta_* = V_{0*} - V'_{0*} = \frac{RT}{F} \ln \left(\frac{c_{*OX}}{c_{*Red}} \right) \quad (5.3)$$

where, V_{0*} is the electrode voltage, V'_{0*} is the formal potential, R is the universal gas constant, F is the Faraday constant, c_{*OX} is the concentration of reactants in a reduction process, and c_{*Red} is the concentration of products (also in a reduction process happening in a cathodic half-cell). A schematic of the constituted near-electrode layers and associated electric potentials are indicated in Fig. (5.1).

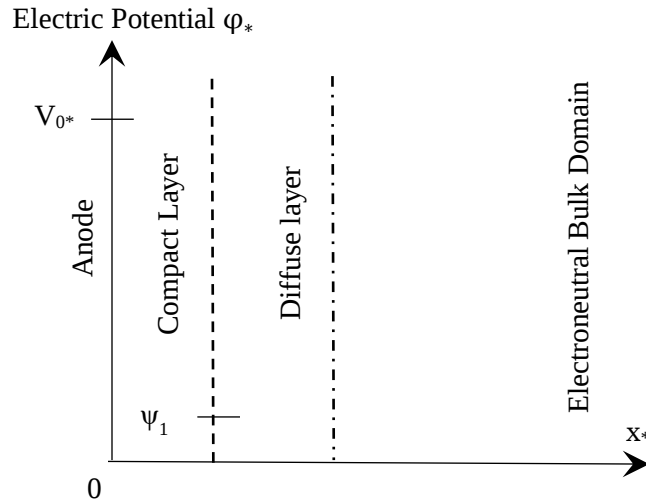


Figure 5.1. Schematic of the constituted layers across the electrode (here anode) and associated electric potentials. x_* coordinate is considered perpendicular to the electrode surface directing outwards.

The formal potential would be equal to the measured potential of the half-cell when the ratio of the concentrations of the oxidized and reduced species is equal to one⁷⁵. In a self-exchange reaction (between the chemical species that are identical except for the oxidation state), the value of the over-potential is zero. However, for an electrode reaction, the value of the over-potential is non-zero³⁶ and determined by Eq. (5.3).

The reorganization factor, λ_{el} , which expresses the energy required to distort the nuclear configuration of the reactants and transforms it into the nuclear configuration of the products without electron transfer, is constituted by the following two terms³⁶:

$$\lambda_{el} = \lambda_i + \lambda_o \quad (5.4)$$

where λ_i represents the ‘inner’ contribution corresponding to the contribution from the reorganization of participating species. This contribution expresses the energy required for changes in the bond lengths. In other words, it is the relaxation energy of the reactant dominated by the short-range bond forces. The inner contribution is calculated using the following relation³⁶:

$$\lambda_i = \sum_{j=1}^M \frac{1}{2} k_j (q_{Ox,j} - q_{Red,j})^2 \quad (5.5)$$

where k_j is the force constant; q_j is the displacement in the normal mode coordinate, and M is the total number of the normal mode coordinates.

A normal mode of a fluctuating system is a pattern of movement, in which all sections of the system move sinusoidally with the same frequency and constant phase relation. The total number of normal modes depends on the molecular structure. If the total number of atoms in a molecule is N , a nonlinear molecule has $M=3N-6$ normal modes. In contrast, a linear molecule has $M=3N-5$

normal modes⁷⁷, because the rotation about the molecular axis cannot be observed, since in a linear molecule all atoms are located along a straight line.

The ‘outer’ contribution, λ_O , in Eq. (5.4) represents the reorganization energy of the solvent dominated by the long-range electrostatic forces⁷⁶. The outer component is calculated as³⁶:

$$\lambda_O = \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{a_O} - \frac{1}{R_O} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_S} \right) \quad (5.6)$$

Here, a_O is the radius of the sphere of the reactant (ions) and R_O is twice the distance from the center of participating species to the electrode (during the electron transfer). Also, ϵ_S is the static dielectric constant (corresponding to low frequencies), and ϵ_{op} is the optical dielectric constant (corresponding to high frequencies). Several experiments have shown that the outer component of the reorganization energy (λ_O) dominates in the liquid-solid interfacial interactions, i.e., in the electrode electron-transfer reactions, and thus, $\lambda_i \ll \lambda_O$ ⁷⁸⁻⁷⁹.

5.3. Computational model and the governing equations

The following computational model is introduced to predict the interface voltage. The model is comprised of the ionic transport equations and Poisson’s equation for the electric potential, i.e., Eqs. (4.41) - (4.43). The solvent dielectric constant ϵ is equal to the static dielectric constant. It should be emphasized that Eqs. (4.41) - (4.43) are used in the diffuse layer, starting at the interface with the compact layer.

To introduce the numerical procedure capable of finding the interface voltage ψ_1 , a computational domain featuring an anode in contact with the electrolyte at rest is sketched in Fig. (5.2). The computational domain starts from the interface of the compact and diffuse layers. Hence,

the electric potential at the interface provides a Dirichlet-type boundary condition for the computational model. The height of the domain, H_* , is 10 μm .

The boundary conditions in the electroneutral bulk read:

$$y_* = 0: \varphi_* = 0, c_*^+ = c_*^- = c_{*\infty} \quad (5.7)$$

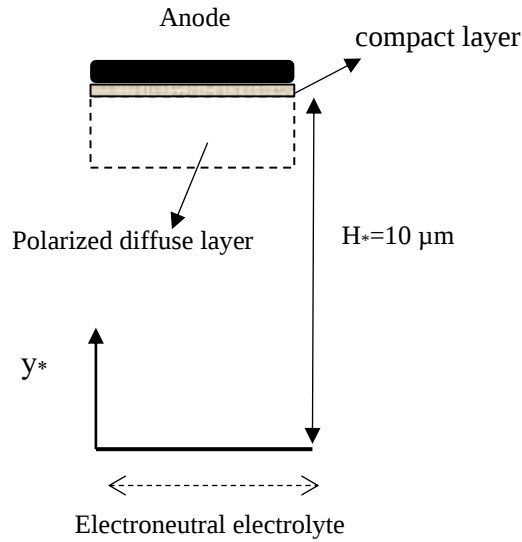


Figure 5.2. The anodic half-cell and the one-dimensional computational domain.

The ionic boundary conditions at the interface of the compact and diffuse layers (i.e., at $y_* = H_*$) are found from relations (3.45) and (3.47). The electric potential boundary condition is ψ_1 . The ionic boundary conditions express that anions are discharged at the anode surface (through the electron transfer) and become neutral molecules. Also, the flux of cations at the anode surface is equal to zero.

In practice, the electrode's voltage is measured and known experimentally, and the voltage at the interface is not known. Here, a numerical algorithm is introduced to predict and correct the interface voltage by employing the Marcus activation energy⁷³ and the Frumkin slow discharge

theory⁸⁰. The Frumkin slow discharge theory yields the following relation⁸⁰ for an electrode with $\eta_* > 0$:

$$\Delta G_* = -F(\alpha - z_{ox})\psi_1 - \alpha F\eta_* \quad (5.8)$$

where, α is the charge transfer coefficient, and z_{ox} is the valence of products in an oxidation reaction ($\text{Red} \rightarrow \text{Ox} + e$). Assuming $\alpha = 0.5$ (symmetric electron transfer reaction) and $z_{ox} = 1$ (1:1 electrolyte), Eq. (5.8) takes the form:

$$\Delta G_* = 0.5F\psi_1 - 0.5F\eta_* = 0.5F(\psi_1 - \eta_*) \quad (5.8)$$

The following algorithm is proposed for the above-mentioned anodic half-cell (a similar algorithm can be applied to a cathodic half-cell) to predict and correct the interface voltage:

(i) Estimate the ratio of c_{*Ox}/c_{*Red} . (ii) Calculate the over-potential from Eq. (5.3). (iii) Calculate the activation energy from Eq. (5.2) using the over-potential value from step (ii). (iv) Using the calculated values of the activation energy and the over-potential in Eq. (5.8), find the interface voltage ψ_1 . (v) Solve the governing equations (4.41) - (4.43) for the anodic half-cell with the bulk boundary conditions (5.7) and the interfacial boundary conditions (3.47)-(3.48). (vi) After the numerical simulation reaches a steady-state solution, recalculate the ratio c_{*Ox}/c_{*Red} at the interface. (vii) Repeat steps (ii) to (iv) to predict the interface voltage ψ_1 . (viii) If the value of ψ_1 predicted at step (vii) matches the one at step (iv) within an acceptable error margin (for example, the absolute difference is less than 0.1 V), the estimated ratio c_{*Ox}/c_{*Red} is accepted, and the corresponding value of ψ_1 is sufficiently accurate. Otherwise, find a new value of ψ_1 by applying an under-relaxation formulation for the old (step (iv)) and predicted ψ_1 (step (vii)) values and repeat the algorithm from step (v) to step (viii). The loop should be repeated until the absolute difference between the old and predicted ψ_1 values is less than the defined error margin.

5.4. Results and discussions

Here, we first apply the Marcus electron transfer theory to the canola oil as the ionic conductor liquid in electrostatic atomization and subsequently employ the proposed numerical algorithm within the developed computational framework to predict the value of the electric potential at the interface.

Canola oil has a nonlinear molecule composed of saturated and non-saturated fatty acids⁸¹. The nonlinear structure is defined as a branched-chain molecule where atoms do not lie along a straight line. The canola oil composition incorporates 56% unsaturated oleic acid with the chemical formula of $C_{18}H_{34}O_2$ (N=54). This provides the total number of normal modes in the canola oil molecule as $M=3N-6=156$. However, this information is redundant because λ_i is negligibly small, as explained in Section (5.2), and need not be calculated.

Considering canola oil as a 1:1 weak electrolyte, one can use the following values of the dielectric properties⁸²: $\epsilon_{op} = 2.946$ and $\epsilon_s = 3.00$. The diameter of the canola oil molecule is 1.4 nm based on the density and molecular weight⁸³. The value R_0 is taken as 1.5 times the canola oil ion diameter. Electron transfer can happen at the electrode surface and at distances extremely close to the electrode⁸⁴, so 1.5 times the ion diameter is considered as an average of the doubled distance between the center of ion participating in electron transfer reaction and the electrode surface.

$$R_0 = 1.5 \times (2a_0) = 2.1 \times 10^{-9} \text{m} \quad (5.9)$$

Then, the reorganization energy of canola oil ions can be evaluated based on Eq. (5.6) as $\lambda_{el} = \lambda_i + \lambda_o \approx \lambda_o = 6.7 \times 10^{-22} \text{J}$. The electric conductivity, σ , of canola oil was measured as¹⁷ $2.6 \times 10^{-11} \text{ S/m}$. The dielectric constant is equal to 3 and the diffusivity is^{85,86} $D = 1 \times 10^{-11} \text{ m}^2/\text{s}$. The charge relaxation time⁸⁷, τ_c , is calculated as $\tau_c = \epsilon\epsilon_0/\sigma = 1 \text{s}$, and the Debye length, λ_D , is found as $\lambda_D = (D\tau_c)^{1/2} = 3.1 \mu\text{m}$. The bulk ion concentration is taken $8 \times 10^{17} \text{ 1/m}^3$ in the following simulations (as before in previous chapters).

The number concentration of canola oil molecules in the bulk (c_{*Bulk}^N) is calculated from the canola oil properties (molecular weight $MW_{Canola} = 0.9 \text{ kg/mol}$ and density of canola oil $\rho_{Canola} = 910 \text{ kg/m}^3$), and Avogadro's number and is found as $6.1 \times 10^{26} \text{ m}^{-3}$. For an oxidation reaction in a 1:1 electrolyte ($\text{Re} \rightarrow \text{Ox} + e$), anions release the extra electron to become neutralized; hence, $c_{*Ox}/c_{*Red} = c_*^N/c_*^-$. The concentration of neutral ions (molecules) at the vicinity of the electrode, c_*^N , is assumed to be only modestly modified by the faradaic reactions and remain close to the bulk neutral concentration; therefore, it is considered to be equal to c_{*Bulk}^N i.e., $6.1 \times 10^{26} \text{ m}^{-3}$.

From our previous experimental measurements, the electric current density, J_{e*} , has been expressed as a function of anode voltage, V_{0*} , in the framework of the Butler-Volmer-Frumkin kinetics as¹⁷:

$$J_{e*} = 10^{\{[V_{0*} - (a_a + \psi_1)]/b_a\}} \left[\frac{\text{A}}{\text{cm}^2} \right] \quad (5.10)$$

where $a_a + \psi_1$ and b_a are the experimental coefficients measured as $0.99996(V_{0*}/2) + 1.05123$ and 0.1118 , respectively. Table (5.1) summarizes the parameter values used in the following simulations for the canola oil as the ionic conductor liquid.

Table 5.1. Model parameters used in the simulations.

Parameter	Value	Reference
Bulk Ion Concentration, $c_{*\infty}$	$8 \times 10^{17} \text{ m}^{-3}$	Calculated
Debye Length, λ_D	$3.1 \times 10^{-6} \text{ m}$	Calculated
Diffusivity, D	$10^{-11} \text{ m}^2 \text{ s}^{-1}$	85, 86
Electric Conductivity, σ	$2.6 \times 10^{-11} \text{ Sm}^{-1}$	17
Faraday Constant, F	$96485.33 \text{ C mol}^{-1}$	36
Neutral Ion Concentration, c_*^N	$6.1 \times 10^{26} \text{ m}^{-3}$	Calculated

Reorganization Energy, λ_{el}	6.7×10^{-22} J	Calculated
Universal Gas Constant, R	$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$	88

Two examples are considered to demonstrate the proposed numerical algorithm for finding the interfacial voltage ψ_1 at two different values of the applied voltage at the electrode. In the first example, considered as case A, the applied voltage at the anode is taken as 500 V. The corresponding anion flux at the electrode surface is calculated from Eq. (5.10) as $|j_*^-| = J_{e*}/e = 1.1 \times 10^{14} \text{ m}^{-2} \text{ s}^{-1}$. Then, the value of the over-potential from Eq. (5.3) is calculated for the anodic half-cell (oxidation reaction $c_*^- \rightarrow c_*^N + e$). If one assumes that, in this case, the order of the concentration of the neutral ions (products) at the interface of the compact and diffuse layers would be three orders of magnitude higher than that of the anions (i.e., as the first guess in the iteration algorithm described above is $c_{*Ox}/c_{*Red} = 10^3$), one obtains from Eq. (5.3):

$$\eta_* = \frac{RT}{F} \ln \left(\frac{c_{*Ox}}{c_{*Red}} \right) = \frac{8.314 \times 300}{96485.33} \ln(10^3) = 0.179 \quad (5.11)$$

Calculating the activation energy of the oxidation reaction using Eq. (5.2) yields:

$$\Delta G_* = N_A \left(\frac{\lambda_{el}}{4} \left[1 - \frac{e\eta_*}{\lambda_{el}} \right]^2 \right) = 6.022 \times 10^{23} \left(\frac{6.7 \times 10^{-22}}{4} \left[1 - \frac{1.6022 \times 10^{-19} \times 0.179}{6.7 \times 10^{-22}} \right]^2 \right) = 176 \frac{\text{kJ}}{\text{mol}} \quad (5.12)$$

Substituting the calculated values of the over-potential η_* and the activation energy ΔG_* into Eq. (5.8), one obtains $\psi_1 = 3.8$ V. Using this value of the interfacial voltage as the boundary condition for the electric potential in the computational domain, the system of Eqs. (4.41) - (4.43) is solved numerically with the previously described bulk boundary conditions.

The boundary conditions at the interface of the compact and diffuse layers are as demonstrated in relations (3.45) and (3.47) with $|j_*^-| = 1.1 \times 10^{14} \text{ m}^{-2} \text{ s}^{-1}$ and $\phi_* = 3.8$ V.

Performing the one-dimensional simulation and following the algorithm described in section (5.3) for the oxidation reaction $c_*^- \rightarrow c_*^N + e$ in a 1:1 electrolyte (canola oil), one obtains $c_*^N/c_*^- =$

$6.1 \times 10^{26} / 6.2 \times 10^{23} = 984$. The over-potential, the activation energy, and the interface voltage found from Eqs. (5.2), (5.3) and (5.8) are 0.179 V, 166 KJ/mol and 3.7 V, respectively. Because the absolute difference between the predicted and calculated interface voltages is not greater than 0.1 V, the assumed value of $c_*^N / c_*^- = 10^3$ at step (i) of the algorithm is considered acceptable and the result converged. Hence, in the case of canola oil in contact with a metallic anode with the applied electrode voltage of 500 V and the anion flux of $1.1 \times 10^{14} \text{ m}^{-2}\text{s}^{-1}$ at the anode surface, the electric potential at the interface between the compact and diffuse layers drops to 3.7 V.

The dimensionless ions concentration c_i and charge density distribution q across the anodic half-cell of case A are depicted in Fig. (5.3). The non-dimensional scales are $c_{*\infty}$ for c_*^+ and c_*^- , $ec_{*\infty}$ for q_* and H_* for y_* . The maximum value of q_* occurs at the interface and is equal to $-1.2 \times 10^5 \text{ Cm}^{-3}$.

The polarized diffuse layer thickness λ_d is also shown in Fig. (5.3) (b).

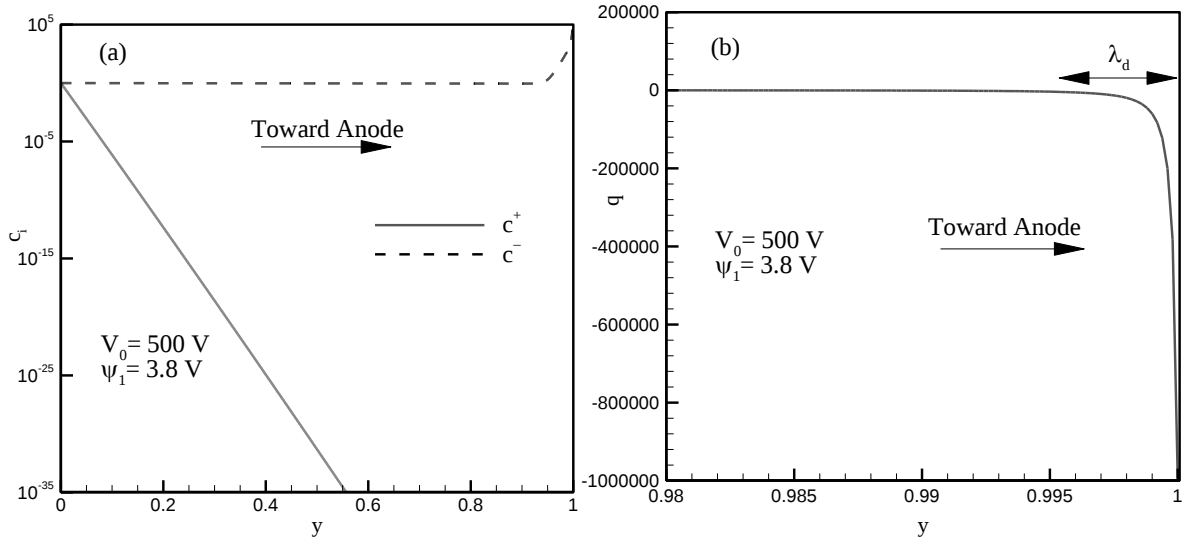


Figure 5.3. Dimensionless ion and charge distributions across the anodic half-cell with $\psi_1 = 3.8 \text{ V}$ and $|j_*^-| = 1.1 \times 10^{14} \text{ m}^{-2}\text{s}^{-1}$: (a) Ions concentration, (b) charge density.

In the second example, considered as case B, the applied voltage at the anode is taken as 1750 V. This voltage yields the anion flux value at the interface equal to $|j_*^-| = 2.975 \times 10^{14} \text{ m}^{-2}\text{s}^{-1}$. Starting from the assumption $c_*^N/c_*^- = 9 \times 10^4$, provides the first guess of interface voltage as 10 V. Taking this value as the interfacial electric-potential boundary condition and solving Eqs. (4.41) - (4.43) numerically yields $c_*^N/c_*^- = 1.7 \times 10^4$. Here, as described above, the c_*^N value is considered constant in all simulations and equal to $6.1 \times 10^{26} \text{ m}^{-3}$. The value of c_*^- at the interface is calculated through the numerical solution of Eqs. (4.41) - (4.43) within the one-dimensional domain in Fig. (5.2).

By employing the c_*^N/c_*^- ratio in Eqs. (5.2) - (5.3) to calculate the over-potential and activation energy values, the predicted interface voltage is found as 7.3 V. Taking this value as the interface voltage and solving Eqs. (4.41) - (4.43) produces negative anion concentration at the interface because the flux of counter-ions due to discharge becomes greater than the accumulation of counter-ions due to electromigration. To prevent this issue, an under-relaxation formulation is introduced to correct the predicted value:

$$\psi_1^{\text{New}} = \psi_1^{\text{Old}} + \beta(\psi_1^{\text{Predicted}} - \psi_1^{\text{Old}}) \quad (5.13)$$

Here, $\psi_1^{\text{Predicted}}$ is the predicted interface voltage, ψ_1^{Old} is the old interface voltage, ψ_1^{New} is the new interface voltage, and β is the under-relaxation factor.

Taking under-relaxation factors close to unity provides situations where the discharge rate is greater than the accumulation of counter-ions which yields negative anion concentrations at the interface. Hence, a low under-relaxation factor ($\beta = 0.18$) is used. This provides the new interface voltage as 9.5 V. By solving Eqs. (4.41) - (4.43), the ratio c_*^N/c_*^- becomes 5.8×10^4 . Employing this value in the over-potential and activation energy formulations and recalculating the interfacial voltage yields the value of 9.6 V. This indicates that the algorithm is converged and the interfacial

voltage for the considered anion flux value $|j_*^-| = 2.975 \times 10^{14} \text{ m}^{-2}\text{s}^{-1}$ and electrode potential $V_{0*} = 1750 \text{ V}$ is found through the proposed procedure. Note that a different choice of the under-relaxation value could have resulted in more iterations to converge to this result.

6. Conclusions and Future Work

This work aims to gain a fundamental knowledge of electrification, constituted near-electrode layers, and the electrohydrodynamic flow inside electrostatic atomizers by providing realistic numerical and theoretical models. The previous models do not demonstrate the electrification mechanism and the constituted near-electrode layers. In this study, distinct theoretical and numerical models are provided to elaborate the charging phenomenon, the constituted compact Stern layer, and internal electrohydrodynamic flow.

The electrification of an ionic conductor liquid in electrostatic atomizers is predicted by accounting for the faradaic reactions at the electrode surface. The numerical approach solves the cation and anion transport equations along with the Poisson equation for the electric potential coupled with the continuity and momentum equations using the OpenFOAM platform. The boundary conditions are modified to account for the faradaic reactions at the liquid/electrode interface. A novel analytical solution for the near-electrode boundary layer with the electric current is found and matched with the analytical solution for the outer layer. The uniformly valid analytical solution for the low-voltage case is used as a benchmark case for the numerical simulations, and the agreement of the analytical and numerical results is established. An additional benchmark case used to validate the numerical results is a two-dimensional flow in a microchannel with a polarizing section without electric current (with the ζ -potential) and electro-osmotic flow driven by the longitudinal external electric field.

The electrification of canola oil flowing through a microchannel is studied with two counter-electrodes that sustain an electric current. Also, the effect of the longitudinal external electric field is studied. The removal of the resulting bulk net electric charge by the flow (the so-called spray current) is predicted. The two contributions to the spray current, the viscous scraping, and the

Smoluchowski slip are compared under the conditions reminiscent of the electrostatic atomizers. It is found that under the realistic values of the longitudinal electric field strength, the viscous scraping is the dominant mechanism for producing the spray current in comparison to the Smoluchowski slip. Both the viscous scraping and the electro-osmosis are equally diminished at a higher viscosity (as follows from the Poiseuille law and the expression for the Smoluchowski slip, both inversely proportional to the viscosity). Accordingly, the dominance of the viscous scraping under the realistic values of the external electric field would be sustained at any viscosity. Because it was shown that the effect of the longitudinal electric field is always negligibly small compared to the viscous scraping, an “electroneutral” liquid would be inevitably collected at the channel exit if one would allow the volumes coming from the upper and lower halves being mixed (for example, by collecting all the liquid in a vessel). Only, separating these volumes at the exit, e.g., by a central separating plate, one would collect charged liquid. It should be emphasized that the flow in the model channel atomizer remains practically unidirectional because the Coulombic body force arising in the electrode section (due to the appearance of the polarized layers) is insufficiently strong under the realistic conditions to reverse the flow near one of the electrodes. In the channel with the insulated walls in the exit section, the spray current value is practically conserved along the channel length.

In this study, a modified model of the compact layer adjacent to a metallic electrode, which carries an electric current is introduced. The model details the ion non-specific adsorption process (first introduced in the seminal work of Stern) as a two-dimensional process, which does not lead to ion discharge in a faradaic reaction only if it is adsorbed onto oxides or impurity islands. Otherwise, on clean metal islands, a faradaic reaction occurs, electrons are transferred, and no

adsorbed ions of the compact-layer type exist. The discharged ions become neutral molecules and leave to be replaced by other discharging ions, thus sustaining the electric current.

This two-dimensional vision of the compact layer can be reduced to the equivalent one-dimensional compact layer model of the Stern layer type (with only monolayer adsorption possible). In addition, the present equivalent one-dimensional compact layer model is generalized to account for the multilayer, Langmuir–Brunauer–Emmett–Teller ion adsorption mechanism. This multilayer equivalent one-dimensional compact layer can be characterized by its thickness and capacitance. Both the thickness and capacitance are predicted rather than used as adjustable parameters. As the adsorption to-desorption ratio β , corresponding to the layers higher than one, increases, the thickness of the equivalent one-dimensional compact layer model λ_s decreases, whereas the capacitance C_s increases. There exists a limiting value of β for which $\lambda_s = 0$ and $C_s = \infty$. The Stern layer thickness can be measured, for example, by X-ray photoelectron spectroscopy (XPS)⁶⁸. The results are intriguing because the measurements reveal that the Stern layer compresses (becomes thinner) as the electrolyte concentration increases. This counterintuitive result is in line with the predictions of the present theory that multilayer ion adsorption makes the equivalent one-dimensional Stern layer thinner because of the accumulation of a higher charge at the compact layer “capacitor” at a fixed potential difference, that is, an increase in the Stern layer capacitance. In more concentrated electrolytes⁶⁸, multilayer ion adsorption is facilitated, and accordingly, the Stern layer becomes thinner.

Applications such as electrostatic atomizers used for charging oils, kerosene, and diesel fuel to facilitate their secondary atomization and finer dispersion as well as multiple electrohydrodynamic devices transporting the so-called dielectric liquids, can benefit significantly from the insight into the nature of the near-electrode compact layer achieved in this work. It is shown that, at high

voltages, the major potential drop occurs at the compact layer²⁷, and the boundary conditions in any theoretical and numerical simulations could be imposed at the interface of the compact and diffuse layers⁴¹. It should be emphasized that liquid charging by means of the so-called charge emission at the tip of a needle electrode in electrospinning, electrospraying, and electrostatic atomization proceeds due to faradaic reactions responsible for the formation of a nearby polarized layer in the ionic conductor liquid, which is issued as a flowing charged liquid jet^{16,17,63,69,70}. It is highly effective due to the high electric field strength near the tip of the electrode; however, it has the same physical nature as in the near-plane electrode zone in model microchannel atomizers⁴¹. The latter case is described by an easier theoretical/numerical description, which is the main reason that it has been studied in detail, whereas the cases with the needle electrodes are more involved, and their numerical investigations are still underway. Note also that because the thickness of the Stern layer is much smaller than any practically possible radius of curvature of the needle electrode tip, the planar theory of the Stern layer holds without any restrictions.

The Frumkin slow discharge theory is used to develop an algorithm to determine the electric potential value at the interface of the compact and diffuse layers formed near the high-voltage electrode during the electrostatic atomization process. Unlike the previous models, the electric potential at the interface is calculated rather than considered to be an ad hoc parameter. Specifically, the proposed numerical approach is capable of calculating the electric potential value at the interface. The computational models for electrokinetics and electrohydrodynamic flow that solve the ionic transport equations require the electric potential value at the interface as a boundary condition. The ionic conductor liquids employed in the electrostatic atomization possess low dielectric constant values. Hence, the entire potential drop across the electric double layer occurs within the compact layer. The sustained electric current at the electrode surface is due to discharge

counterions through faradaic reactions. These reactions at the electrode surface are kinetics-limited, which allows the application of the Frumkin slow discharge theory. The activation energy is calculated from the Marcus electron transfer theory. The ionic transport equations and the Poisson equation are solved numerically in a 1D computational domain starting from the electroneutral bulk toward the interface of the compact and diffuse layers. The ionic boundary conditions at the interface account for the flux of counterions, which has been measured experimentally. Two cases with different applied voltages at the electrode and counterion flux values revealed that the proposed approach could predict the corresponding interfacial voltage.

In the present work, the method of calculation of the potential ψ_1 from first principles is proposed. As a result, the entire electrokinetic theory could describe experiments without any adjustable parameters in a self-consistent way. Accordingly, any comparison with the experiment which reveals agreement without an adjustable parameter involved would indirectly confirm the theory, including the predicted values of the voltage drop.

For future work, the theoretical and numerical models presented in this thesis can be applied to a realistic domain with higher dimensions to predict the spray current in practical cases. However, it requires a high-performance computing infrastructure. Besides, the numerical model can become dimensionless to avoid the necessary super-fine resolution at the electrode vicinity by choosing appropriate scales.

Appendix A

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Kashir, B., Perri, A., Yarin, A., Mashayek, F.: Slow discharge theory and calculation of the potential drop across the compact layer at high electrode voltages. **Langmuir** 35, 14458-14464 (2019)



Slow Discharge Theory and Calculation of the Potential Drop across the Compact Layer at High Electrode Voltages

Author: Babak Kashir, Anthony E. Perri, Alexander L. Yarin, et al

Publication: Langmuir

Publisher: American Chemical Society

Date: Nov 1, 2019

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Kashir, B., Perri, A., Yarin, A., Mashayek, F.: Theoretical and numerical study of formation of near-electrode layers in electrostatic atomization. **Langmuir** 35, 11080-11088 (2019).



Theoretical and Numerical Study of Formation of Near-Electrode Layers in Ionic Conductor Liquids at High Voltages

Author: Babak Kashir, Anthony E. Perri, Farzad Mashayek, et al

Publication: Langmuir

Publisher: American Chemical Society

Date: Aug 1, 2019

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References

- [1] Yule, A. J., Shrimpton, J. S., Watkins, A. P., Balachandran, W., Hu, D. Electrostatically atomized hydrocarbon sprays. *Fuel* **1995**, 74, 1094-1103.
- [2] Kourmatzis, A., Allen, J., Shrimpton, J. S. Electrical and spray characteristics of a multi orifice charge injection atomizer for electrically insulating liquids. *Atomization Spray* **2010**, 20, 269-280.
- [3] Rigit, A., Shrimpton, J. S. Spray characteristics of charge injection electrostatic atomizers with small-orifice diameters. *Atomization Spray* **2006**, 16, 421-442.
- [4] Shrimpton, J. S., Laoonual, Y. Dynamics of electrically charged transient evaporating sprays. *Int. J. Numer. Meth. Eng.* **2006**, 67, 1063-1081.
- [5] Taylor, I. Electrically driven jets. *Proc. R. Soc. London Ser. A.* **1969**, 313, 453-475.
- [6] Melcher, J. R. "Electrohydrodynamics," in *Thirteenth International Congress on Theoretical and Applied Mechanics*, edited by E. Becker and G. K. Mikhailov (Springer, New York, 1973), pp. 240-263.
- [7] Melcher, J. R. Taylor, G. I. Electrohydrodynamics: A review of the role of interfacial shear stresses. *Annu. Rev. Fluid Mech.* **1969**, 1, 111-146.
- [8] Saville, D. A. Electrohydrodynamics: The Taylor-Melcher leaky dielectric model. *Annu. Rev. Fluid Mech.* **1997**, 29, 27-64.
- [9] Chang, H-C., Yeo, L. Y. *Electrokinetically Driven Micro Fluidics and Nano Fluidics*. Cambridge University Press, New York, **2010**.
- [10] Green, N. G., Ramos, A., Gonzalez, A., Morgan, H., Castellanos, A. Fluid flow induced by nonuniform ac electric fields in electrolytes on microelectrodes I. Experimental measurements. *Phys. Rev. E.* **2000**, 61, 4011-4018.

- [11] Bazant, M. Z., Thornton, K., Ajdari, A. Diffuse-charge dynamics in electrochemical systems. *Phys. Rev. E*. **2004**, 70, 021506(1)-021506(24).
- [12] Dutta, P., Beskok, A. Analytical solution of combined electroosmotic/pressure driven flows in two-dimensional straight channels: Finite Debye layer effects. *Anal. Chem.* **2001**, 73, 1979-1986.
- [13] Dutta, P., Beskok, A., Warburton, T. C. Numerical simulation of mixed electroosmotic/pressure driven micro flows. *Numer. Heat Transfer, Part A*. **2002**, 41, 131-148.
- [14] Shrimpton, J. S. *Charge Injection Systems-Physical Principles, Experimental and Theoretical Work*. Springer, Berlin, **2009**.
- [15] Zhang, Y., Yarin, A. L. Electric current and irreversible faradaic reaction on electrode in contact with electrolyte. *J. Electrochem. Soc.* **2012**, 159, H787-H791.
- [16] Sankaran, A., Staszal, C., Sahu, R. P., Yarin, A. L., Mashayek, F. Evidence of faradaic reactions in electrostatic atomizers. *Langmuir* **2017**, 33, 1375-1384.
- [17] Sankaran, A., Staszal, C., Mashayek, F., Yarin, A. L. Faradaic reactions' mechanisms and parameters in charging of oils. *Electrochim. Acta* **2018**, 268, 173-186.
- [18] Perez, A. T., Traore, P., Koulova-Nenova, D., Romat, H. Numerical study of an electrohydrodynamic plume between a blade injector and a flat plate. *IEEE Trans. Dielectr. Electr. Insul.* **2009**, 16, 448-455.
- [19] Traore, P., Daaboul, M., Louste, C. Numerical simulation and PIV experimental analysis of electrohydrodynamic plumes induced by a blade electrode. *J. Phys. D: Appl. Phys.* **2010**, 43, 225502(1)-225502(8).

- [20] Wu, J., Traore, P., Louste, C., Koulova-Nenova, D., Romat, H. Direct numerical simulation of electrohydrodynamic plumes generated by a hyperbolic blade electrode. *J. Electrostat.* **2013**, 71, 326-331.
- [21] Yan, Z., Louste, C., Traore, P., Romat, H. Velocity and turbulence intensity of an EHD impinging dielectric liquid jet in blade-plane geometry. *IEEE Trans. Ind. Appl.* **2013**, 49, 2314-2322.
- [22] Traore, P., Wu, J., Louste, C., Pelletier, Q., Dascalescu, L. Electrohydrodynamic plumes due to autonomous and nonautonomous charge injection by a sharp blade electrode in a dielectric liquid. *IEEE Trans. Ind. Appl.* **2015**, 51, 2504-2512.
- [23] Luo, K., Wu, J., Yi, H-L., Tan, H-P. Three dimensional finite amplitude electroconvection in dielectric liquids. *Phys. Fluids* **2018**, 30, 023602(1)-023602(16).
- [24] Kilic, M. S., Bazant, M. Z., Ajdari, A. Steric effects in the dynamics of electrolytes at large applied voltages. I. Double-layer charging. *Phys. Rev. E* **2007**, 75, 021502(1)-021502(16).
- [25] Kilic, M. S., Bazant, M. Z. Ajdari, A. Steric effects in the dynamics of electrolytes at large applied voltages II. Modified Poisson-Nernst-Planck equations. *Phys. Rev. E* **2007**, 75, 021503(1)-021503(11).
- [26] Chu, K. T., Bazant, M. Z. Electrochemical thin films at and above the classical limiting current. *SIAM J. Appl. Math.* **2005**, 65, 1485-1505.
- [27] Bazant, M. Z., Chu, K. T., Bayly, B. J. Current-voltage relations for electrochemical thin films. *SIAM J. Appl. Math.* **2005**, 65, 1463-1484.
- [28] Bazant, M. Z., Kilic, M. S., Storey, B. D., Ajdari, A. Towards an understanding of induced-charge electrokinetics at large applied voltages in concentrated solutions. *Adv. Colloid Interface Sci.* **2009**, 152, 48-88.

- [29] Lopez-Herrera J. M., Popinet, S., Herrada, M. A. A charge conservative approach for simulating electrohydrodynamic two-phase flows using volume-of-fluid. *J. Comput. Phys.* **2011**, 230, 1939-1955.
- [30] Rubinstein, I., Shtilman, L. Voltage against current curves of cation exchange membranes. *J. Chem. Soc., Faraday Trans. 2.* **1979**, 75, 231-246.
- [31] Yossifon, G., Chang, H-C. Selection of nonequilibrium overlimiting currents: Universal depletion layer formation and vortex instability. *Phys. Rev. Lett.* **2008**, 101, 254501(1)-254501(4).
- [32] Rubinstein, I., Zaltzman, B. Electro-osmotically induced convection in a permselective membrane. *Phys. Rev. E* **2000**, 62, 2238-2251.
- [33] Rubinstein, I., Zaltzman, B., Lerman, I. Electroconvective instability in concentration polarization and nonequilibrium electro-osmotic slip. *Phys. Rev. E* **2005**, 72, 011505(1)-011505(19).
- [34] Zaltzman, B., Rubinstein, I. Electro-osmotic slip and electroconvective instability. *J. Fluid Mech.* **2007**, 579, 173-226.
- [35] Antropov, L. I. *Theoretical Electrochemistry*. Honolulu University Press of the Pacific, Honolulu, **2001**.
- [36] Bard, A. J., Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*. John Wiley & Sons, New York, **2001**.
- [37] Levich, V. G. *Physicochemical Hydrodynamics*. Prentice-Hall, Englewood Cliffs, 1962.
- [38] Cherepanov, G. P. *Mechanics of Brittle Fracture*. McGraw-Hill, New York, 1979.
- [39] Frumkin, A. Adsorptionerscheinungen und elektrochemische kinetic. *Z. Elektrochem. Angew. Phys. Chem.* **1955**, 59, 807–822.

- [40] Bonnefont, A., Argoul, F., Bazant, M. Z. Analysis of diffuse-layer effects on time-dependent interfacial kinetics. *J. Electroanal. Chem.* **2001**, 500, 52–61
- [41] Kashir, B., Perri, A. E., Yarin, A. L., Mashayek, F. Numerical investigation of ionic conductor liquid charging at low to high voltages. *Phys. Fluids* **2019**, 31, 021201.
- [42] Stern, O. Zur theorie der elektrolytischen dopperezpelschicht. *Z. Elektrochem. Angew. Phys. Chem.* **1924**, 30, 508–516.
- [43] Grahame, D. C. The electrical double layer and the theory of electrocapillarity. *Chem. Rev.* **1947**, 41, 441–501.
- [44] Helmholtz, H. Studien über electrische Grenzschichten. *Ann. Phys.* **1879**, 243, 337–382.
- [45] Smoluchowski, M. On the theory of electric cataphoresis and surface conduction. *Phys. Z.* **1905**, 6, 529–531.
- [46] Werkhoven, B. L., Everts, J. C., Samin, S., van Roij, R. Flow induced surface charge heterogeneity in electrokinetics due to stern layer conductance coupled to reaction kinetics. *Phys. Rev. Lett.* **2018**, 120, 264502(1)-264502(6).
- [47] Tsirlina, G. A., Petrii, O. A., Nazmutdinov, R. R., Glukhov, D. V. Frumkin correction: microscopic view. *Russ. J. Electrochem.* **2002**, 38, 154–163.
- [48] Kuznetsov, A. M., German, E. D. *Elektrokhimiya* **1990**, 26, 835–866.
- [49] Marcus, R. A. Electron transfer reactions in chemistry. Theory and experiment. *J. Electroanal. Chem.* **1997**, 438, 251–259.
- [50] Karniadakis, G. E., Beskok, A., Aluru, N. *Microflows and Nanoflows, Fundamentals and Simulation*. Springer, New York, **2005**.
- [51] van Dyke, M. *Perturbation Methods in Fluid Mechanics*. Parabolic Press, Stanford, 1975.
- [52] Hinch, J. E., *Perturbation Methods*, Cambridge University Press, Cambridge, 1991.

- [53] Weller, H. G., Tabor, G., Jasak, H., Fureby, C. A tensorial approach to computational continuum mechanics using object-oriented techniques. *Comput. Phys.* **1998**, 12, 620–631.
- [54] George, A., Liu, J. W. *Computer Solution of Large Sparse Positive Definite Systems*. Prentice-Hall, Englewood Cliffs, 1981.
- [55] Perez, E. E., Carelli, A. A., Crapiste, G. H. Temperature dependent diffusion coefficient of oil from different sunflower seeds during extraction with hexane. *J. Food Eng.* **2011**, 105, 180–185.
- [56] He, R., Chen, S., Wu, B. Dynamic diffuse double-layer model for the electrochemistry of nanometer-sized electrodes. *J. Phys. Chem. B* **2006**, 110, 3262–3270.
- [57] Przybylski, R., Mag, T., Eskin, A. M., Mc Donald, B. E., “Canola oil” in Bailey’s *Industrial Oil and Fat Products*, edited by F. Shahidi and A. E. Bailey (John Wiley & Sons, New York, 2005), Vol. 2.
- [58] Schnitzer, O., Yariv, E. The Taylor-Melcher leaky dielectric model as a macroscale electrokinetic description. *J. Fluid Mech.* **2015**, 773, 1-33.
- [59] Reznik, S. N., Yarin, A. L., Zussman, E., Bercovici, L. Evolution of a compound droplet attached to a core-shell nozzle under the action of a strong electric field. *Phys. Fluids* **2006**, 18, 062101(1)-062101(13).
- [60] Langmuir, I. The constitution and fundamental properties of solids and liquids. Part I. Solids, *J. Am. Chem. Soc.* **1916**, 38, 2221–2295.
- [61] Brunauer, S.; Emmet, P.H.; Teller, E. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **1938**, 60, 309–319.
- [62] Jeans, J. *The Mathematical Theory of Electricity and Magnetism*. Cambridge, Cambridge University Press, **1958**.

- [63] Yarin, A.L., Pourdeyhyimi, B., Ramakrishna, S. *Fundamentals and Applications of Micro- and Nanofibers*. Cambridge, Cambridge University Press, **2014**.
- [64] Israelachvili, J.N. *Intermolecular and Surface Forces*. New York, Elsevier, **2011**.
- [65] Gradshteyn, I.S., Ryzhik, I.M. *Table of Integrals, Series and Products*. Elsevier, **2014**.
- [66] Guiochon, G., Felinger, A., Shirazi, D. G., Katti, A. M. *Fundamentals of preparative and nonlinear chromatography*. Amsterdam, Elsevier, **2006**.
- [67] Fehlner, L.P. The adsorption of oxygen on discontinuous metal films. In *1965 Transactions of the Third International Vacuum Congress*. Stuttgart, Germany (Adam, H., Editor); Pergamon Press, Oxford, **1967**; Vol. 2, Part III, pp. 691-703.
- [68] Brown, M.A.; Goel, A.; Abbas, Z. Effect of electrolyte concentration on the Stern layer thickness at a charged interface. *Chem. Int. Ed.* **2016**, 55, 3790–3794.
- [69] Malkawi, G.; Yarin, A. L.; Mashayek, F. Breakup mechanisms of electrostatic atomization of corn oil and diesel fuel. *J Appl. Phys.* **2010**, 108, 064910(1)-064910(6).
- [70] Theron, S.A.; Zussman, E.; Yarin, A.L. Experimental investigation of the governing parameters in the electrospinning of polymer solutions. *Polymer* **2004**, 45, 2017-2030.
- [71] Kashir, B.; Perri, A. E.; Yarin, A. L.; Mashayek, F. Theoretical and numerical study of formation of near-electrode layers in electrostatic atomization. *Langmuir* **2019**, 35, 11080–11088.
- [72] Marcus, R.A. Chemical and electrochemical electron-transfer theory. *Ann. Rev. Phys. Chem.* **1964**, 15, 155-196.
- [73] Marcus, R.A. Electron transfer reactions in chemistry. Theory and experiment. *Rev. Mod. Phys.* **1993**, 65, 599-610.
- [74] Zeng, Y., Bai, P., Smith, R. B., Bazant, M. Z. Simple formula for asymmetric Marcus-Hush kinetics. *J. Electroanal Chem.* **2015**, 748, 52-57.

- [75] Ho, J., Coote, M. L., Cramer, C. J., Truhlar, D. G. Theoretical calculation of reduction potentials. In *Organic Electrochemistry: Revised & Expanded 5th Edition*. Hammerich, O., Speiser, B., Eds.; CRC Press, Florida, **2016**; pp. 229-259
- [76] Bazant, M. Z., Bai, P. Charge transfer kinetics at the solid-solid interface in porous electrodes. *Nat. Commun.* **2014**, 5, 3585 (1)-3585 (7).
- [77] Landau, L.D., Lifshitz, E. M. *Mechanics (3rd Edition)*. Pergamon Press, **1976**.
- [78] Henstridge, M.C., Laborda, E., Rees, N. V., Compton, R. G. Marcus-Hush-Chidsey theory of electron transfer applied to voltammetry: A review. *Electrochim. Acta* **2012**, 84, 12-20.
- [79] Baranski, A. S., Winkler, K., Fawcett, W. R. New experimental evidence concerning the magnitude of the activation parameters for fast heterogeneous electron transfer reactions. *J. Electroanal. Chem.* **1991**, 313, 367-375.
- [80] Tsirlina, G. A., Kuznetsov, O.A., Petrii, O. A., Yu, I. Effect of the electrical double layer on the rate of electrode processes at high over-voltages: comparing different theoretical approaches. *Russ. J. Electrochem.* **1999**, 35, 832-840.
- [81] Gunstone, F. *Fatty acid and lipid chemistry*. Blackie, London, **1996**.
- [82] Shah, Z. H., Tahir, Q. A. Dielectric properties of vegetable oils. *J. Scientific Research* **2011**, 3, 481-492.
- [83] Sahasrabudhe, S. N., Rodriguez-Martinez, V., O'Meara, M., Farkas, B. E. Density, viscosity and surface tension of five vegetable oils at elevated temperatures: Measurement and modeling. *Int. J. Food Prop.* **2017**, 20, 1965-1981.
- [84] Gavaghan, D. J., Feldberg, S. W. Extended electron transfer and the Frumkin correction. *J. Electroanal. Chem.* **2000**, 491, 103-110.

- [85] Perez, E. E., Carelli, A. A., Crapiste, G. H. Temperature-dependent diffusion coefficient of oil from different sunflower seeds during extraction with hexane. *J. Food Eng.* **2011**, 105, 180-185.
- [86] Fernandez, M. B., Perez, E. E., Crapiste, G. H., Nolasco, S. M. Kinetic study of canola oil and tocopherol extraction: Parameter comparison of nonlinear models. *J. Food Eng.* **2012**, 111, 682-689.
- [87] Yarin, A. L., Lee, M. W., An, S., Yoon, S. S. *Self-Healing Nanotextured Vascular Engineering Materials*. Springer Nature, Switzerland AG, Cham, **2019**.
- [88] Jensen, W. B. The universal gas constant R. *J. Chem. Educ.* **2003**, 80, 731-732.

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Projects

- Design, fabrication and laboratory test of distinct non-premixed burners in laminar and turbulent fluid flow regimes
- Study the effect of preheating and diluting on combustion pollutants in non-premixed burners
- Conduct comprehensive numerical simulations (large-eddy simulations and Reynolds averaged simulations) on non-premixed reacting flows employing OpenFOAM platform
- Employ deep learning semantic segmentation techniques to extract features such as shock and vortical structures in fluid flows
- Conduct theoretical research on charging mechanism inside electrostatic atomizers
- Develop and validate multiple numerical flow solvers for charge injection and electrohydrodynamic flow employing OpenFOAM platform
- Conduct numerical study on transport phenomena inside electrostatic atomizers
- Solving a coupled system of non-linear equations related to inter-atomic forces present in compact layer with MATLAB and Mathematica software
- Conduct analytical research on electrically-driven fluid flows
- Conduct a numerical study on the effect of the ventilation system on the propagation of Covid-19 viruses inside the dentistry clinic at UIC

Education

Jan. 2016 – Jan. 2021

Doctor of Philosophy in Mechanical Engineering (Ph.D.)

University of Illinois at Chicago, Chicago, Illinois, USA

Ph.D. Thesis: A Theoretical and numerical study on electrification and flow inside electrostatic atomizers

Sep. 2005 – March 2008

Master of Applied Science in Aerospace Engineering (M.Sc.)

Amirkabir University of Technology (Tehran Polytechnic), Tehran, IRAN

M.Sc. Thesis: Experimental and numerical study on preheating and diluting effects in non-premixed flames of methane and propane

Sep. 2001 – Sep. 2005

Bachelor of Applied Science in Mechanical Engineering (B.Sc.)

University of Kerman, Kerman, IRAN

B.Sc. Thesis: Study on the Operation of Deaerators in thermal power plants

Publications and Presentations:

Journal Papers (peer-reviewed):

[1] **Kashir, B.**, Tabejamaat, S., Baigmohammadi, M.: Experimental study on propane/oxygen and natural gas/oxygen laminar diffusion flames in diluting and preheating conditions. **Thermal Science** 16, 1043-1053 (2012)

Impact Factor: 1.54

[2] **Kashir, B.**, Tabejamaat, S., Baigmohammadi, M.: An experimental study of the stability of natural gas and propane turbulent non-premixed flames under diluting condition. **Thermal Science** 16, 1055-1065 (2012)

Impact Factor: 1.54

[3] **Kashir, B.**, Tabejamaat, S.: A numerical study on the effects of H₂ addition in non-premixed turbulent combustion of C₃H₈-H₂-N₂ mixture using a Flamelet approach. **International Journal of Hydrogen Energy** 38, 9918-9927 (2013)

Impact Factor: 4.08

[4] Baigmohammadi, M., Tabejamaat, S., **Kashir, B.**: A numerical study on the effects of hydrogen addition levels, wall thermal conductivity, and inlet velocity on methane/air premixed flame in a micro reactor. **Energy Equipment and Systems** 2, 103-119 (2014)

Impact Factor: ---

[5] **Kashir, B.**, Tabejamaat, S., Jalalatian, N.: A numerical study on combustion characteristics of blended methane-hydrogen bluff-body stabilized swirl diffusion flames. **International Journal of Hydrogen Energy** 40, 6243-6258 (2015)

Impact Factor: 4.08

[6] **Kashir, B.**, Tabejamaat, S., Jalalatian, N.: The impact of hydrogen enrichment and bluff-body lip thickness on characteristics of blended propane/hydrogen bluff-body stabilized turbulent diffusion flames. **Energy Conversion and Management** 103, 1-13 (2015)

Impact Factor: 7.18

[7] **Kashir, B.**, Tabejamaat, S., Jalalatian, N.: On large eddy simulation of blended CH₄-H₂ inverse diffusion flames: The impact of hydrogen concentration on thermal and emission characteristics. **International Journal of Hydrogen Energy** 40, 15732-15748 (2015)

Impact Factor: 4.08

[8] **Kashir, B.**, Perri, A., Yarin, A., Mashayek, F.: Numerical investigation of ionic conductor liquid charging at low to high voltages. **Physics of Fluids** 31, 021201(1)- 021201(17) (2019)

Impact Factor: 2.62

[9] **Kashir, B.**, Perri, A., Yarin, A., Mashayek, F.: Theoretical and numerical study of formation of near-electrode layers in electrostatic atomization. **Langmuir** 35, 11080-11088 (2019).

Impact Factor: 3.68

[10] Jalalatian, N., Tabejamaat, S., **Kashir, B.**, EidiAttarzadeh, M.: An experimental study on the effect of swirl number on pollutant formation in propane bluff-body stabilized swirl diffusion flames. **Physics of Fluids** 31, 055105(1)-055105(16) (2019)

Impact Factor: 2.62

[11] **Kashir, B.**, Perri, A., Yarin, A., Mashayek, F.: Slow discharge theory and calculation of the potential drop across the compact layer at high electrode voltages. **Langmuir** 35, 14458-14464 (2019)

Impact Factor: 3.68

[12] Perri, A., Sankaran, A., **Kashir, B.**, Staszal, C., Schick, R., Mashayek, F., Yarin, A.: Electrically-driven toroidal Moffat vortices: Experimental observations. **Journal of Fluid Mechanics** 900, A12(1)-A12(17) (2020)

Impact Factor: 2.9

[13] **Kashir, B.**, Ragone, M., Ramasubramanian, A., Yurkiv, V., Mashayek, F.: Application of fully convolutional neural networks for feature extraction in fluid flow. **Journal of Visualization** (Accepted)

Impact Factor: 0.95

[14] Ragone, M., Yurkiv, V., Ramasubramanian, A., **Kashir, B.**, Mashayek, F.: Data driven estimation of electric vehicle battery state-of-charge informed by automotive simulations and multi-physics modeling. **Journal of Power Sources** 483, 229108(1)-229108(12) (2021)

Impact Factor: 8.247

Conference Papers (peer-reviewed):

[1] **Kashir, B.**, Tabejamaat, S.: A Numerical Investigation of Turbulence-Chemistry-Radiation Interaction in CH₄/H₂/N₂ Jet Diffusion Flames. **Eighth Mediterranean Combustion Symposium**, Cesme, Turkey (2013)

[2] **Kashir, B.**, Tabejamaat, S., Jalalatian, N.: The impact of swirl intensity and hydrogen enrichment on the hybrid CH₄-H₂ bluff-body stabilized swirl flame. **Ninth Mediterranean Combustion Symposium**, Rhodes, Greece (2015)

[3] Sankaran, A., Staszal, C., **Kashir, B.**, Perri, A., Yarin, A., Mashayek, F.: Electrostatic atomization: Effect of electrode materials on electrostatic atomizer performance. **69th Annual Meeting of the APS Division of Fluid Dynamics**, Portland, Oregon (2016)

[4] **Kashir, B.**, Perri, A., Sankaran, A., Staszal, C., Yarin, A., Mashayek, F.: A numerical study on liquid charging inside electrostatic atomizers. **69th Annual Meeting of the APS Division of Fluid Dynamics**, Portland, Oregon (2016)

[5] **Kashir, B.**, Perri, A., Yarin, A., Mashayek, F.: A numerical study on charging mechanism in leaky dielectric liquids inside the electrostatic atomizers. **70th Annual Meeting of the APS Division of Fluid Dynamics**, Denver, Colorado (2017)

[6] **Kashir, B.**, Perri, A., Schick, R.J., Yarin, A., Mashayek, F.: A computational model for liquid charging in electrostatic atomizers. **14th International Conference on Liquid Atomization and Spray Systems**, Chicago, Illinois (2018)

[7] **Kashir, B.**, Perri, A., Yarin, A., Mashayek, F.: A numerical study on the effect of the electrode voltage on the near-electrode layers in leaky dielectric liquids. **71st Annual Meeting of the APS Division of Fluid Dynamics**, Atlanta, Georgia (2018)

[8] Jalalatian, N., **Kashir, B.**: A numerical study on NO emission in bluff-body stabilized swirl diffusion flames. **71st Annual Meeting of the APS Division of Fluid Dynamics**, Atlanta, Georgia (2018)

- [9] **Kashir, B.**, Perri, A., Yarin, A., Mashayek, F.: Electrification mechanism and constituted near-electrode layer inside electrostatic atomizers. **29th Conference on Liquid Atomization and Spray Systems**, Paris, France (2019)
- [10] Mashayek, F., **Kashir, B.**, Perri, A., Yarin, A.: Stern compact layer in ionic conductor liquid charging. **72nd Annual Meeting of the APS Division of Fluid Dynamics**, Seattle, Washington (2019)
- [11] **Kashir, B.**, Ragone, M., Yurkiv, V., Mashayek, F.: Data-driven prediction of vortical structures in turbulent flows employing deep learning techniques. **72nd Annual Meeting of the APS Division of Fluid Dynamics**, Seattle, Washington (2019)
- [12] Ragone, M., Yurkiv, V., Ramasubramanian, A., **Kashir, B.**, Mashayek, F.: Data-driven estimation of electric vehicle battery state of charge informed by multi-physics modeling. **ECS Meeting Abstracts** 02, 1598 (2020)
- [13] Ragone, M., Yurkiv, V., Ramasubramanian, A., Anahideh, H., **Kashir, B.**, Shahbazian-Yassar R., Mashayek, F.: Data-driven approach for predicting thermal runaway in Li-Ion battery. **ECS Meeting Abstracts** 02, 818 (2020)

Journal Article Reviewing:

- International Journal of Hydrogen Energy 1 paper
Publisher: Elsevier Impact Factor: 4.08
- Physics of Fluids 5 papers
Publisher: American Institute of Physics Impact Factor: 2.62
- European Journal of Computational Mechanics 1 paper
Publisher: River publishers Impact Factor: ---

Google Scholar link (citations)

https://scholar.google.com/citations?hl=en&user=LBU7gkQAAAAJ&view_op=list_works&sortby=pubdate

Total Citations: 85

H index: 6

National Awards

- University of Illinois student champion on XSEDE national supercomputer

<https://www.xsede.org/community-engagement/campus-champions/domain-and-student-champions#student>

Professional Experience and Membership

- **Research Assistant, Turbulence and Combustion Research Laboratory**
Amirkabir University of Technology, Tehran, IRAN, Sep. 2007 – Dec. 2015
 - Design, fabrication and laboratory test of distinct non-premixed burners
 - Conduct numerical research on reactive flows employing OpenFOAM platform

- **Research Assistant, Computational Multiphase Transport Research Laboratory**

The University of Illinois at Chicago, Chicago, Illinois, USA, Jan. 2016 – Present

- Responsible for employing deep learning techniques to extract features of turbulent flows
- Conduct research on numerical modeling of flow and charging mechanism inside electrostatic atomizers employing OpenFOAM platform

Professional Academic Membership

- **Member of the International Combustion Institute, March 2014 – Present**
- **Member of the American Physical Society, June 2015 – Present**

Teaching Experience

Teacher Assistant, Aerospace Engineering Department, Amirkabir University of Technology

- Advanced Fuel and Combustion I (Graduate Course)
- Advanced Fuel and Combustion II (Graduate Course)
- Heat Transfer (Under-graduate Course)

Teacher Assistant, Mechanical Engineering Department, University of Illinois at Chicago

- Internal Combustion Engines (Graduate Course)
- Air Pollution Control (Graduate Course)
- Senior Design Undergraduate Course)

Computer Skills:

- CFD software: Fluent, OpenFOAM
- Programming software: Fortran, C++, Mathematica, Python, Shell Scripting
- Post Processing software: Paraview, Tecplot
- Operating system: Ubuntu, Windows
- Mesh Generation software: Gambit, OpenFOAM
- Deep Learning Library: Pytorch, Keras

Fields of Interest:

- Electrostatic Atomization
- Deep Learning
- Turbulence
- Combustion
- Computational Fluid Dynamics
- Heat Transfer

- Parallel Processing
- Object-Oriented Programming (C++)

References:

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