A FUNDAMENTAL STUDY ON WATER DROPLETS COALESCENCE ON ELECTROWETTABLE SURFACES IN AIR AND DIESEL MEDIA

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DEDICATION
TO
My beloved parents
Saeed and Um-abid
And my beloved wife
Aziza
And my beloved kids
Tolana, Aseel, and Solaf
ABSTRACT

Electrowetting phenomena have been implemented in many applications. Biomedical fields, for example, use devices that employ electrowetting phenomena in lab-on-a-chip devices. In this research endeavor, though, electrowetting phenomena were studied for other potential applications. Electrowetting phenomena were intensively studied on coated surfaces. The surfaces were coated using different coating techniques. The coated surfaces were characterized for their effects on contact angle modulation, which is governed by electrowetting phenomena. In addition, small droplets transport on coated surfaces was achieved by virtue of gradient coatings and electrowetting phenomena.

Electrowetting phenomena were used to initiate coalescence of water drops that are close vicinity. Electrocoalescence of water drops on coated surfaces was driven by contact angle modulation via electrowetting effects. Electrocoalescence of water drops was studied in both air and diesel media. These phenomena were experimentally investigated by using high-speed imaging photography. This study included experimental investigations on a coalescer prototype.
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CHAPTER I

INTRODUCTION

1.1 Introduction

Understanding the provisions, at which coalescence of water droplets in immiscible media occurs, is important for designing coalescers, separators, and filter media. Numerous conditions can accelerate or prevent coalescence in all different kinds of separation media. Any separator has to be carefully designed for specific applications in order to get the highest performance possible. The mechanisms of how separators function can vary tremendously.

The scope of this work is to setup the stage for a new separator prototype that is based on enhanced coalescence via electrical forces. In order to design a new kind of coalescers, a careful study of the design parameters has to be made. Fundamental understanding of the physics behind the working principal is a crucial step for a successful design. The new design is based on coalescence of water droplets on engineered surfaces. On these surfaces, mainly two phenomena synergize and trigger coalescence; these two phenomena are electrowetting and electrocoalescence.
1.2 Electrowetting and electrocoalescence

Electrowetting is a phenomenon where the wetting property of a liquid to a solid surface can be altered by introducing electrical potential to the non-wetting solid interface. Electrical forces change the apparent contact angle of the liquid to the solid in a controllable fashion. Conditions, parameters, and other related issues pertaining to electrowetting are discussed in the body of this manuscript.

Electrocoalescence is a phenomenon in which coalescence (i.e. merging) of droplets take place by virtue of electrical forces. In this research, electrocoalescence takes place as an effect of electrowetting phenomena. Criteria for electrocoalescence to take place in different media are demonstrated in Chapters V and VII.

1.3 Motivation

Coalescence of water droplets is the key factor to the separation of water present in immiscible media. Different mechanisms lead to coalescence, some of which are rigorously investigated, while basic understanding of other mechanisms is still lacking. To this date, mechanisms and criteria for coalescence of water droplets accompanied by electrowetting phenomena are not well understood and need be investigated. The outcome of investigating these phenomena helps in choosing the right parameters when building separation devices.
One of the major processes industries invest in is fuel cleanliness. Regulations set by governments makes the task of cleaning (i.e. filtering) fuels even more challenging. To meet government’s standards, more efficient, reliable, cost effective separation techniques are yet to be developed. However, when designing a new separator prototype, it is not practical to jump from the basic knowledge of electrowetting phenomena to the design of the separator without paying attention to the details of the physics of the phenomena.

It is then, very important to study the electrowetting and electrocoalescence phenomena in air as well as liquid (i.e., diesel fuel). Studying these phenomena in air medium facilitate the interpretation of the results of the phenomena for the electrowetting system in general, while studying these phenomena in diesel medium give a clear picture of how does the performance varies in other immiscible fluids.

1.4 Hypothesis

- Electrowetting phenomena causes water droplets to coalesce via contact angle controllability.
- In Secondary emulsions, coalescence of water droplets can be accelerated by virtue of the added electrical forces.
- Coalescence can be achieved in relatively high speeds in electrowetting configurations compared to conventional means.
1.5 Objectives

In order to investigate on the applicability of electrowetting in coalescence of water droplets present in diesel medium, the electrowetting system has to be custom designed to meet the criteria for coalescence in a compact separator. Electrode materials, dielectric materials, voltage sources, in addition to other parameters have to be studied intensively. The following will be included in the study:

- Electrowetting configurations.
- Air and diesel as immiscible media.
- Choice of dielectric material.
- Coating methods.
- Electrodes materials.
- Drop size ranges.
- Power source types and modes.
- Speed of coalescence.

1.6 Organization of the manuscript

This research is a multidisciplinary research project. This section is devoted to help the reader navigate through the manuscript with ease. Herein, the chapters will be listed, and a short description of what is included in the chapters is provided.
Chapter I

In this chapter, as was demonstrated earlier, an overview of the research goals, hypotheses, motivation, objectives are stated. In addition to, introducing the variables that were studied in much detail, to the reader.

Chapter II

In this chapter, definitions, terminology, and the-state-of-the-art on related topics are demonstrated. The focus of this chapter is on short-range forces that pertain to electrowetting and electrocoalescence phenomena. Also, a brief overview of what has been done, by other researchers, in these two fields of study is presented.

Chapter III

In this chapter, the experimental setups and the equipment used in the investigations are described. The electrical components used for electrowetting experiments are also demonstrated. Different setups for electrowetting experiments and different coating techniques were used and are described in this chapter. Equipment used for generating high-resolution images and high-speed frame rates were used and are described in details. Two particle sizer systems facilitated generating drop size distributions; advantages and limitations of the equipment are presented.
Chapter IV

Coatings were applied to substrates by two different techniques, the first was by spin coating and the second was by dip coating. Depending on the technique used for the coating, the films on the substrates had different morphologies; these morphologies were identified and characterized and are presented in this chapter.

Chapter V

Contact angle reduction induced by electrowetting can be affected by the surrounding medium. Air medium is the focus in this chapter; setting up the experiments was relatively easy and accessible for all electrowetting configurations in air medium. Contact angle reduction driven by the electrode orientation is discussed in this chapter.

Chapter VI

Electrode orientation and coating gradient had effects not only on the contact angle reduction, but also on the droplet stability. Droplets were moved by virtue of electrical forces, in addition to other factors that initiated the droplets movements, which are discussed in this chapter. Cases where droplets moved on the coated substrates are presented and discussed in this chapter, too.
Chapter VII

Multiple electrode orientation and two continuous phase media were used for electrowetting experiments. In this chapter, the diesel medium was the continuous phase while water drops were the discrete phase. Due to the big difference between air and diesel fluid properties, it was expected that the electrowetting phenomena would be different in diesel medium. The same methodology used for characterizing electrowetting performance in air media was followed for the diesel medium case. Results pertaining to diesel medium experiments are discussed in this chapter.

Chapter VIII

All introduced phenomena synergize and lead to the coalescence of water droplets on the coated substrates. In this chapter, a coalescer design is introduced. The performance of the coalescer, and critiques on the coalescer are given in this chapter.

Chapter IX

Conclusions and general suggestions on selected topics are provided in this chapter. In this research project, there were areas of high potential applications that can be extended for further gain of knowledge and hence, implementation.
CHAPTER II

LITERATURE REVIEW

2.1 Introduction

In this chapter, an overview of the important topics that are directly related to electrowetting and electrocoalescence phenomena will be briefly demonstrated. Formulation of the equations that represent electrowetting, theoretically, will be briefly presented without the fine details.

2.2 Interfacial energies

In micro scale world, short-range forces become important, while, other forces such as gravity gradually diminish, as the particle sizes get smaller. When studying a system of more than one phase, it is useful to quantify the intermolecular forces that act between/among phases, at least to the macroscale level in terms of accessible quantities. Surface tension, interfacial tension, and surface energy are terms given to distinguish the energies for the different combinations of solid/liquid/gas interfaces. Surface tension and interfacial tension are sometimes used interchangeably.
2.2.1 Young’s equation

The interaction between different phases that are in physical contact is a complicated phenomenon. Fundamentals of these interactions are not discussed in this thesis and can be found elsewhere (1–4). An abstraction of these interactions can be represented by Young’s equation. Young’s equation (1) relates the interfacial energies of a three-phase system. A system consisting of solid, liquid, and gas interacts in a way that is determined by the intermolecular structure at the three-phase contact line. Typically, this interaction can be symbolized by a sessile liquid drop sitting on a solid surface and surrounded by gas medium, as shown in Figure 2.1.

![Figure 2.1 A schematic of a hypothetical sessile droplet surrounded by gas medium and sitting on a solid substrate. The schematic shows a characteristic contact angle, which forms at the three-phase contact line. Interfacial energies are also shown; the interfacial energies represent the interaction between the phases solid, liquid and gas.](image)

Young’s equation states the relation between the interfacial energies and is given by equation 2.1 (5–9). In this relation, \( \theta \) is the theoretical equilibrium contact angle. The theoretical “ideal” equilibrium contact angle is rarely
accessible experimentally (10). In general, there are factors that affect the discrepancies in the experimental values of the contact angle of a specific liquid on a specific surface. Morphology of the investigated surface can have great effects on the equilibrium contact angle measurements (11, 12). Droplet evaporation has effects on the equilibrium contact angle, as well (13, 14). One other factor that influences the equilibrium contact angle is the droplet’s sorption into the substrate (15, 16). Young’s equation is

$$\cos \theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$$  \hspace{1cm} (2.1)

where, $\gamma_{LG}$ is the surface tension of the liquid droplet. $\gamma_{SL}$ is the solid-liquid interfacial energy. $\gamma_{SG}$ is the solid surface energy.

Despite the fact that the ideal equilibrium contact angle can’t be precisely identified, there are plenty of methods for measuring the contact angle. A commonly used method is by evaluating the three-phase contact line from images of sessile drops for advancing and receding contact angles. In the following section, the techniques for measuring the contact angles based on imagery will be reviewed. Furthermore, in the subsequent section, a brief review about the advancing and receding contact angles measurements will be given.
2.2.2 Contact angle measurements

In literature, the contact angle calculation for sessile droplets was often times conducted solely based on the shape of the droplets, and in other times based on the shape of the droplet as well as the physical properties of the droplet. With the advancements of the computational power that the computerized systems posses, specialists in the field of contact angle measurements and computerized computation developed plug-ins that helps in calculating the contact angle.

There are two methods for contact angle measurements, the first one is based on analytical-image processing and the second one is based on exclusively image processing (17, 18). The analytical-image processing technique depends not only on the shape of the drop, but also on other physical properties such as surface tension and density of the drop (19). For the second method, the contact angle is measured based on the shape of drop only, regardless of its physical properties. The mathematical models that were used for these calculations can be found elsewhere (20, 21). In a nutshell, the plug-in software algorithm identifies the counter lines of the outer boundaries of the droplet, and based on that, a contact angle value is reported. One important factor that determines the accuracy of the contact angle calculation is the quality of the image. In addition, the view angle can lead to false contact angle measurements (22). Figure 2.2 shows a proper setup for measuring the contact angle for the side-view method.
2.2.3 Contact angle hysteresis

The equilibrium contact angle is a unique quantity dictated by the interfacial energies stated previously in Young’s relation. However, as mentioned earlier the equilibrium contact angle is almost impossible to measure experimentally. It has been proposed that the equilibrium contact angle can be approximated by taking the average of the advancing and receding contact angles measurements (23). The method of advancing and receding contact angle measurements are used to assess the degree of variation in the intrinsic contact angle. There are different approaches for measuring the advancing and receding contact angles. Some techniques rely on the measurements of the dynamically changing contact angles, while other techniques consider only the static contact angles. In the case of the dynamic contact angle measurement, the triple contact point moves slowly while taking the contact angle measurement.
The triple contact point is the point where the three phases meet depicted in Figure 2.1. In the static contact angle measurement method, the triple contact point is presumably fixed and thus the contact angle measured in this case is the static contact angle.

One method for measuring the advancing contact angle is by adding small volume increments to a sessile drop and measuring the contact angle as the triple contact point advances with less than 1mm/min advancing velocity (24). This advancing velocity is appropriate for low viscous fluids such as water. Whereas, for high viscous fluids such as crude oils and hydrocarbons, the contact angle is dependent on the advancing velocity and care must be taken to account for this effect (25). Another approach is to consider the maximum static contact angle as the advancing contact angle(26). A third approach is to measure the contact angle on inclined surfaces(27).

The receding contact angle can be found in the same way the advancing contact angle is obtained, except that the drop volume is reduced by using a withdrawal micro syringe (28). In all cases, regardless of the method used for obtaining the advancing and receding contact angles, the hysteresis is defined as the difference between the advancing and receding contact angles (29–32). The demonstrated methods for obtaining the contact angles were for the sessile drop method, and it is worth mentioning that there are other methods for obtaining the contact angles, but they are beyond the scope of this work. The reader should
refer to the literature for the advancements on the field of contact angle measurement studies (33–43). The concept of hydrophobicity and hydrophilicity will be introduced next.

2.2.4 Hydrophobicity and hydrophilicity

For solid surfaces the hydrophobic/hydrophilic interaction with water is a well-established field of study. In the macro scale level, the interaction between water molecules and the solid surface molecules are manifested in the contact angle that a water droplet forms with the solid surface. The chemistry behind these interactions can be found elsewhere (44–50). It has to be noted that the contact angle is not solely a function of these hydrophobic/hydrophilic interactions, but also synergistically affected by the interfacial energies shown earlier in Young’s relation. One common way of characterizing solid surfaces based on water contact angle is by describing the solid surface as hydrophobic or hydrophilic surface. Hydrophobic surfaces have contact angles of 90° or less, while hydrophobic surfaces have contact angles greater than 90° (51, 52). Figure 2.3 shows water drops on the hydrophobic surface of a plant leaf, as an example from nature.
2.2.5 Bond number

The Bond number ($B_0$) is a dimensionless quantity that quantifies the magnitude of surface tension forces relative to body forces, and is given by equation 2.2 (53–57). Depending on the two-phase system physical properties, the dimensionless quantity can be calculated for a given two-phase system.

\[
B_0 = \frac{\Delta \rho gd^2}{\gamma}
\]  

(2.2)

where, $\Delta \rho$ is the difference in mass densities between the two phases. $g$ is the gravitational acceleration. $d$ is a characteristic length determined by the drop size in the case of sessile water drops.
For water droplets with approximately 2 mm diameter and less, the Bond number is much smaller than unity. Hence, interfacial forces are dominant over the body forces. The surface tension tends to minimize the surface energy and hence tends to make the droplet spherical for $Bo < 1$. Furthermore, the shape of the droplet as well as the contact angle is determined by Young’s interfacial tensions.

2.3 Electrowetting phenomena

Electrowetting is defined as the electrically induced wetting. Electrical forces acts on both, the electrically conducting media and the electrically insulating media in electrowetting configurations. Historically, electrowetting phenomena theory evolved from more basic fundamental science. Electrowetting phenomena are very complicated, and it is not intended to give a thorough review of the formulation of these theories. The fundamental science of these phenomena is not reviewed here, and can be found in literature (2, 58–64).

Electrowetting systems, in general, consist of two main components. The first component is a conducting non-wetting liquid. The second component is a two-electrode configuration. A generic electrowetting system is shown in Figure 2.4 and 2.5. In general, when a droplet is imbedded between the two-electrode systems; the inherent interfacial forces of the two-phase system govern the shape of the droplet. It is assumed that the top wire electrode can be configured in a way that minimizes its effects on the shape of the droplet. Without the
presence of external electrical stresses, the ions are spontaneously distributed in the droplet. With the application of an external electrical potential between the two electrodes and across the droplet, on the other hand, the ions tend to migrate towards the oppositely charged electrodes. The bottom electrode is insulated and the electrical double layer that forms in the insulator/liquid interface is responsible for contact angle modulation, the reader can find more information in the literature for detailed analysis (65–67).

Young’s equation is the result of a balance of surface forces acting on the drop in the absence of the effects by gravitational and electrical forces. In electrowetting the presence of the charges cause electrical forces that must be included in the overall force balance. This additional force causes the drop to deviate from the spherical shape and results in a change in the observable contact angle.
Figure 2.4 A side view of water droplet sitting on a coated electrode, and touching the top electrode. Typically, the droplet is sitting on a hydrophobic layer with a contact angle higher than 100°. The electric potential difference between the two electrodes is zero. The ions in water droplets are randomly distributed inside the droplet.

Figure 2.5 A side view of water droplet imbedded between two electrodes. The bottom flat electrode is coated with a hydrophobic layer and the top wire electrode is not coated. After applying an electrical potential across the drop, the solid flat surface changes from non-wetting state to a partially wetting state. When the electrical potential difference between the electrodes is set back to zero volt, the hydrophobic surface return back to its initial hydrophobic nature.
2.3.1 Young-Lippmann’s equation

Lippmann equation gives a relation between the solid-liquid interfacial tension and the surface charge density, represented in equation 2.3 (68, 69). The change in the solid-liquid interfacial tension is related to the surface charge density, \( \sigma \), and the electrical potential differential.

\[
\sigma = \frac{\partial \gamma_{SL}}{\partial V}
\]  \hspace{1cm} (2.3)

The effective solid-liquid interfacial tension (\( \gamma_{SL} \)) is divided into a chemical part, (\( \gamma_{SL}^0 \)), and electrical-dependent part (\( \gamma_{SL}^V \)), as shown in Equation 2.4 (70, 71).

\[
\gamma_{SL} = \gamma_{SL}^0 + \gamma_{SL}^V
\]  \hspace{1cm} (2.4)

The electrical-dependent part can be obtained from equation 2.3. By rearranging and combining equations 2.1, 2.3, and 2.4; and assuming that the contribution from introducing the electrical potential dominates at the insulator/liquid interface, one can derive the Young-Lippmann relation given by equation (2.5) (72–79).

\[
\cos \theta_V = \cos \theta + \frac{1}{2d} \frac{\varepsilon \varepsilon_r}{\gamma_{LG}} V^2
\]  \hspace{1cm} (2.5)
where $\theta_V$ is the apparent contact angle with the applied voltage. $\theta$ is the inherent contact angle without the presence of the applied voltage. $\varepsilon, \varepsilon_r$ are the permittivity of vacuum and the relative dielectric constant of the insulating layer, respectively. $V$ is the applied voltage, and $d$ is the thickness of the insulating layer.

2.3.2 Contact angle saturation

The Young-Lippmann equation applies under conditions that the applied voltage difference is below the saturation limit (80–82). The saturation limit depends on the electrical properties of the system and the dielectric layer properties in particular (83). The reader is advised to consult the literature for more detailed analysis on the contact angle saturation (84, 85). Despite the fact that contact angle saturation phenomena is not well understood, it can be experimentally observed and quantified in electrowetting systems (86).

2.3.3 Contact angle hysteresis in electrowetting systems

Contact angle hysteresis in electrowetting systems is an inevitable outcome that accompanies electrowetting systems. Hysteresis in electrowetting is more complicated than the hysteresis caused by the intrinsic physical properties of the substrate. The cause of the hysteresis is the way the electrical charges are introduced and accumulated in the substrates (87–89). The introduced charge, through the voltage bias to the substrates causes the contact
angle change. However, when the voltage difference is reset back to zero a portion of the electrical charge retained in the substrate (90, 91). As a result, this retained charge exerts a residual electrical force on the droplet that prevents the drop shape from returning to its initial zero voltage shape and the contact angle does not return to its original zero voltage angle. The difference between the initial and final angles is the contact angle hysteresis due to electrowetting.

Since the contact angle hysteresis is a measure of the degree of variation between two states (i.e. advancing and receding, for instance), there is no global value for hysteresis in electrowetting systems. The reason behind that is due to the fact that there are varieties of initial and final states for contact angle. For example, at each voltage there is a contact angle corresponds to that voltage, and each voltage can be obtained by two mechanisms. The first mechanism is the ramping up from 0 volt to that particular voltage. The second mechanism is the decrease in voltage from a higher voltage to a lower voltage. Hence, the contact angle may differ in these two states at each voltage. For this reason, voltage versus contact angle change loops are sometimes used for demonstrating hysteresis in electrowetting systems (92). Hysteresis also depends on the thickness of the insulator film (93). Hysteresis can be either high, up to 10° or as low as 1.9°(94), depending on the electrical properties of the dielectric. Another factor is the superhydrophobicity of the insulating dielectric. As the dielectric insulator approaches that of a superhydrophobic surface, with contact angles greater than 150°, the hysteresis effect becomes more noticeable.
(95). Superhydrophobicity has other implications on the electrowetting phenomena, such as the reversibility issues of the contact angle with the applied voltage(96). Sometimes hysteresis can be advantageous, such as in droplet movement actuation applications (97, 98). The reader can find more detailed analysis on contact angle hysteresis in electrowetting systems (99–103).

2.3.4 Dielectric breakdown

Dielectric breakdown voltage is defined as the maximum voltage that the polymeric film can withstand without losing its insulating properties (104). Dielectric breakdown may take place through weak spots, defects, or by exceeding a threshold voltage (105). All insulating materials have a voltage threshold limit dictated by their electronic structure (106). The breakdown voltage of the polymeric films also can be affected by their thickness (107). The breakdown voltage can be investigated by the current-voltage characteristics test (108, 109). Theories and investigations on the voltage breakdown phenomena can be found elsewhere (110–119).

In electrowetting systems, the contact angle saturation was suggested to be associated with dielectric breakdown (120). Hence, depending on the dielectric property of the hydrophobic layer, a second dielectric film is often used in a multilayer configuration to increase the electrical breakdown voltage of the hybrid coating (121). This hybrid coating allows for contact angle modulation with the added voltage without reaching the breakdown voltage. In contrast, when
using only one coating with a low dielectric breakdown voltage, a surge of current flow can occur and electrolysis reactions can be easily observed through bubble formation (122). Hence, a two-layer dielectric coating is often used to enhance the electrowetting system performance.

2.4 Electrowetting applications

The ability of contact angle modulation by electrical forces gave rise to varieties of applications in many fields. For example, liquid zoom lens technology has implemented electrowetting for changing the focal length by controlling the wettability of the liquid via electrowetting (123). In biomedical applications, electrowetting was used for droplet transport in lab-on-chip platforms (124, 125). Electrowetting was also used in the so-called Electrowetting display (EWD) technologies (126, 127). In addition to many other applications (128–132).

2.5 Coalescence phenomena

Coalescence is the process in which two or more droplets (or bubbles) merge to form one united droplet. Coalescence phenomena are very complicated, and can’t be explained by a universal law. Depending on the continuous phase physical and chemical properties, and the discreet phase properties many theories were developed to predict coalescence phenomena in different systems. There are similarities, though, between coalescence phenomena when regarded in different systems.
2.5.1 Emulsification processes

Emulsification is the process in which an insoluble or partially soluble phase distributes as fine droplets in another phase to form an emulsion. In general, emulsions are thermodynamically unstable and coalescence occurs spontaneously (133). There are many techniques for producing emulsions from two immiscible phases. Theoretical prediction of drop size distribution aided by experimental results has been successfully made and reported in literature. Simulations including Population Balance Equation (PBE) and Volume-of-Fluid (VOF) methods were used for the theoretical prediction of the drop sizes (134–137). Experimentally, one of the techniques used to generate a narrow distribution of droplet size, is by membrane emulsification (138). Another technique for preparing emulsions is by microfluidization and ultrasonication (139). A third method for making emulsions is by continuous agitation of the immiscible mixture (140–143). In the continuous agitation method, there are many parameters that can effect the drop size distribution. For example, the stirring speed is one parameter that can affect the uniformity of the drop size distribution (144). One of the problems that can be encountered when making emulsions is the phase inversion problem. Depending on the kinetics of the dispersion, the continuous phase may become the discrete phase depending on the dispersed drops break-up rate (145, 146).
2.5.2 Coalescence mechanisms

There are many factors that can promote or hinder coalescence of droplets in an emulsion. First, in order for droplets to coalesce, they have to be in close vicinity. That alone, does not guarantee coalescence. There are two prerequisites, the first one is the interstitial film drainage and the second one is the film rupture (147). Film drainage and rupture can be hindered by a number of factors (148–150). For example, after establishing the liquid bridge between two adjacent drops, capillary forces favor coalescence while viscous forces prevents it (151). Also the flow field containing the dispersed drops can have effects on coalescence of drops. Extensive studies were conducted on colliding drops in different flow fields for investigating the critical conditions for coalescence (152–155).

Coalescence of drops can be hindered by intentionally modifying the emulsion composition. Such emulsions are regarded as stable emulsions. One technique for stabilizing an emulsion is by adding colloidal particles to the emulsion (156, 157). Another way of stabilizing emulsions is by adding surface-active-agents (surfactant)(158–161).
2.6 Filtration techniques

Phase separation of immiscible phases can be achieved by different mechanisms. One of the common methods for achieving the separation of two immiscible phases is by coalescing filters (162). The mechanism of achieving separation depends on the nature of the immiscible phases. There are advantages and disadvantages of using coalescing filters. The details are numerous and can be found elsewhere (163–167).

Enhancing coalescence of drops as a step towards filtration was done by several approaches. Different energy sources that provide the emulsion with an external energy input were used for coalescing droplets. For example, acoustic fields were implemented for initiating coalescence of drops (168, 169). Another example is by using an applied external electrical field. In the next section, snapshots on the use of electrical fields as coalescence enhancers will be given.

2.7 Electrocoalescence

Electrocoalescence is the term used for the electrically triggered coalescence phenomena. The electrical field has been known to enhance coalescence of drops in oil production since 1911 (170). The technology at that time used strong electrical fields for initiating coalescence in relatively low dielectric media. Since then, the idea of using electrical field for coalescing drops has evolved and advanced. Briefly, the electrical fields modify the drop-drop interactions in favor of coalescence. Numerous studies on the effects of electrical
field on suspensions were conducted and can be found elsewhere (171–178). The studies were sometimes theoretical while in other times they were experimental.

2.8 Concluding remark

In this chapter, the basic knowledge on the important aspects of the related topics was briefly reviewed. Advances on the relevant subjects will be given in the related field of study in each chapter.
CHAPTER III

EXPERIMENTAL SETUPS AND CHARACTERIZATION TECHNIQUES

3.1 Introduction

In this chapter, the essential components for the investigations that were carried out in this research endeavor will be briefly demonstrated. There were a lot of similarities between experimental setups; this is the reason for this consolidation. The main parts that were shared between experiments are demonstrated generically in this chapter. More emphasis on each experimental setup will be demonstrated in the relevant chapter whenever is needed. Also, the equipment that were used for characterizing the performance of the observed phenomena will be briefly described in this chapter. Specific details about related issues will be discussed in Appendices.

3.2 Electrode configurations

Electrowetting experiments can be conducted in many different configurations. In this work, three configurations were carefully chosen to better understand electrowetting phenomena. These configurations were, in occasions, to study the effects of the coatings on contact angle change with the presence of
the electrical field. In other occasions, other configurations were used to simulate certain application. These configurations will be demonstrated in details in the following sections.

3.2.1 Vertical wire electrode configuration

The vertical wire electrode configuration consists of a flat surface and a wire electrode perpendicular to the flat surface and separated by a controlled vertical distance. Figure 3.1 shows a schematic of the vertical wire electrode configuration for electrowetting experiments. The spacing between the vertically oriented wire and the flat surface can be controlled via a Plexiglas holder that will be shown later.

Figure 3.1 Side view of a droplet sitting on a coated flat electrode. The top wire electrode is protruding the droplet to a specified distance controlled by a Plexiglas holder (not shown). Electrowetting phenomena can be observed for the vertical wire arrangement in either air media or in diesel media using this setup.
3.2.2 Horizontal electrode configuration

The horizontal electrode configuration consists of a horizontal electrode wire and a flat electrode surface as shown in Figure 3.2. The gap distance between the horizontal wire electrode and the flat surface electrode can be controlled using the Plexiglas holder shown in Figure 3.3 and 3.4. Details about the drawings and dimensions that were used for fabricating the Plexiglas holder are given in Appendix B.

Figure 3.2 Side view of the horizontal wire electrode arrangement used for electrowetting and electrocoalescence experiments. The gap between the horizontal wire electrode and the flat surface electrode can be adjusted using the Plexiglas holder. The top horizontal electrode touches the outer surface of the droplet, hence, making a physical contact with the droplet.
Figure 3.3 Side view of water droplet on a coated surface. The Plexiglas holder is used to control the separation distance between the top wire electrode and the bottom flat surface electrode. The screws are used to control the separation distance between the wire electrode and the flat surface electrode by adjusting them separately.

Figure 3.4 a perspective view of the Plexiglas holder in the horizontal electrode arrangement. The top wire electrode touches the droplet from above. This holder was modified with a fifth screw (to the right) to better control the horizontal orientation of the top wire electrode. In addition, this screw allows for tilting the horizontal electrode at very small angles.
The horizontal electrode configuration was used to study the electrowetting phenomena as well as to other phenomena. In particular, electrocoalescence and droplet movement on coated surfaces, phenomena. Electrocoalescence phenomena were studied, for the most part, using the horizontal electrode arrangement as will be presented in Chapters V, VI and VII. This arrangement was used in both air and diesel media. Droplet movements on coated surfaces were studied using this arrangement in air media as will be presented in Chapter VI.

3.2.3 Parallel flat surfaces electrode configuration

The parallel flat surfaces configuration consists of two flat surfaces parallel to each other and separated by a small gap as shown in Figure 3.5. This electrode configuration was used for both electrowetting and drop movement experiments. More details about droplet movement study will be presented in Chapter VI. Either the flat electrodes can be coated to study a particular phenomenon as desired.
In general, all these electrode configurations were used with different experimental setups. The discreet phase in all cases was water drops, while, the continuous phase varied from being air media and diesel media. In the upcoming chapters, it will be indicated in each experimental investigation the combination of electrode materials and configuration that was used for that particular investigation.

3.3 Power sources

In electrowetting and electrocoalescence experiments, supplied power to the experiments is a very important control parameter. For this reason, reliable powering systems were used. The voltages were in occasions applied to the drops either in a slew rate mode or in a sudden step change mode. The slew rate mode is defined as the rampage in voltage over a period of time. The rampage in
voltage was applied by using a programmable power supply. The sudden step change in voltage is defined as an instant change in the voltage applied to the electrowetting experiments. The sudden step change in voltage was applied using a relay power switch.

3.3.1 Programmable power supply

A programmable power supply was used in several experimental investigations. The programmable power supply was purchased from Chroma, aka QuadTech Inc, Marlborough, MA, USA. The programmable power supply can output a DC voltage ranging from 0-600 VDC. It also can output two kinds of signals simultaneously with the output voltage power. The first kind of signal is an analog signal, and the second one is a digital signal. These signals can be programmed by the user to implement them for different purposes as desired. A picture of the power supply is presented in Figure 3.6.

Figure 3.6 Programmable power supply used for powering electrowetting and electrocoalescence experiments. The power supply outputs the voltage that was used for powering the electrowetting experiments. It also outputs an analog signal as well as a digital signal as defined by the user. The keypad is used to input multiple programming functions as desired by the user.
The first kind of signal was an analog signal as mentioned earlier. The analog and the digital signal were employed in many experimental protocols. The analog signal is a variable 0 to 5 volt signal and was programmed to represent the actual output voltage that is to be applied to the drops, which was ranging from 0-600 VDC. This signal was fed into a data acquisition system. In the data acquisition system, the analog signal was converted to a digitized signal using a microprocessor. The microprocessor converts the analog signal into a digitized signal. The converted signal was then processed by computer interface with MATLAB software package. The frequency at which the data was transferred to the computer was approximately 1 kHz. This means that the signal can be read and represented in 1-millisecond intervals. The reason for tracking the voltage ramp down to millisecond was due to the fact that many experiments were analyzed depending on the voltage that was applied at each moment in time. Voltage calibration and more details about converting the analog signal, to precisely represent the output voltage, are presented in Appendix D. An image of the data acquisition system is presented in Figure 3.7.
Figure 3.7 Data acquisition system for measuring the output voltage of the programmable power supply. The power supply outputs an analog signal corresponds to the output voltage of the power supply. The analog signal is sent to the microprocessor for digital conversion. The converted signal is sent to the computer to be represented graphically into digital bits. Finally, the graphical representation of the bits versus time (in millisecond) can be converted to the actual output voltage by using a calibration curve.

Figure 3.8 and 3.9 show the time needed for the voltage to ramp from 0 volt to the desired set voltage. The output voltage linearly correlated with time for the voltages below 380 VDC. As an example, for the 300 VDC case, Figure 3.8 show this linear correlation. At higher voltages, though, the applied voltage ramp slightly changes with time. Figure 3.9, shows this change in slope as the voltage exceeds 380 VDC.
Figure 3.8 Two cycles of the voltage slew rate of 300 VDC. The rate of change in voltage is linearly correlated with time. The two cycles represent the reproducibility of the voltage slew rate, given that the voltage was allowed to settle back to 0 volts before the second cycle starts.

Figure 3.9 Two cycles of voltage slew rate for 600 VDC. More time is needed to reach the set voltage of 600 volts. Each cycle show that the change in voltage passes through a slightly different ramping rate. The two cycles represent consistent results.
The second kind of signal was a digital signal, as stated earlier. The digital signal was programmed to output in either 0 or 5-volt modes. 0 volt digital signal represents 0 volt output power, while 5-volt digital signal represents any output voltage greater than 0 VDC. This method insures that the power that is provided to the electrowetting experiments can be precisely identified at each moment in time, being 0 VDC or a value greater than 0 VDC. This was one goal of using the digital signal. The second goal of using the digital signal was the ability of powering a low power light source, for a function that will be explained later. Hence, this signal was used to power a light-emitting diode (LED). The LED was used to light a portion of the imaged drops. This is important for accurately identifying the reference time for applying the voltage when analyzing the recorded images of the drops. It is also important for the trigger function that starts the recording of the images at exactly 0 reference time and just above 0 VDC applied to the drops. More clarification about the function of the LED is presented in Chapter V.

3.3.2 Relay power switch

In some occasions a sudden step change in voltage was used to study electrowetting phenomena. A programmable relay power switch was used to give a sudden step change in voltage. The relay power switch and the DC power supply used for these experiments are presented in Figure 3.10. The relay can be programmed using built-in knobs for low frequency ranges. The relay is powered by using a 110 AC volt source. The relay is connected between a DC
power supply and the electrowetting experiment. The relay works as variable switch, following the program defined earlier by the user. The relay is fed with the output voltage power of the DC power supply, to provide electrowetting experiment with whatever the set voltage in the DC power supply is. More details about the relay power switch circuitry and working principal will be presented in Appendix D.

![Relay switch mounted on DC power supply](image)

Figure 3.10 A relay switch is mounted on a DC power supply to provide a sudden step change in voltage used for powering the electrowetting experiment. The voltage is preset using the knobs on the power supply and the relay is programmed at a specific frequency.

3.4 Electrode materials and dimensions

The wire electrodes used in the vertical and horizontal electrode arrangements was a copper wire, 128 μm in diameter with volume resistivity of $1.87 \times 10^{-8} \Omega \cdot m$. Two kinds of flat surfaces were used, the first one was stainless
steel plate with volume resistivity of $7 \times 10^{-7} \Omega \cdot m$ and the second one was indium tin oxide (ITO) coated glass slides. The ITO glass slides were purchased with a transparent semiconducting coating on them. They were purchased from (Sigma Aldrich, St. Louis, MO, USA) with surface resistivity of 100-150 $\Omega$/sq. The flat surfaces (either stainless steel or ITO glass slides) were cut into different dimensions as needed. The dimensions of the flat surfaces differed according to the intended experimental investigation, and they will be stated in the relevant experiments in the relevant chapters of this thesis.

The copper wire electrodes were also used for establishing connection with the flat surfaces to the power supply terminals. The copper wires were attached to substrates using a conducting silver paste. The silver paste had higher conductivity than the electrodes used for the experiments, this is to insure that there is no potential drop occurring due to electrical connections. The silver paste was purchased from (SPI Supplies, West Chester, PA, USA).

3.5 Imaging techniques

For studying the behavior of water drops subjected to electrical potentials in electrowetting experiments, different imaging techniques were used. Depending on the purpose of the imagery, the proper imaging technique was chosen. For example, in contact angle study the Drop Shape Analyzer was used for generating the images of the electrified drops.
3.5.1 Drop Shape Analyzer (DSA)

The DSA was a very helpful tool that was available for precisely measuring the contact angle of the electrified drops. It is equipped with a CCD camera that is capable of producing a high magnification images with high definition. It is also capable of recording videos, automatically, of the observed phenomena for later playback and analysis. From the recorded videos, one can analyze the contact angle change for the entire video using an automated function. An image of the DSA is shown in Figure 3.11.

![Image of the DSA for observing electrowetting and electrocoalescence phenomena.](image)

Figure 3.11 The DSA for observing electrowetting and electrocoalescence phenomena. The CCD camera can produce images with high magnification and high definition of the observed drops. The light source is facing the camera to allow for backfield illumination. The DSA is equipped with an automated syringe dispenser for reproducible drop sizes.

The DSA system is equipped with a software package that allows for automatic video recording. The user has to define a pixel value for triggering the recording. The software *listens* for a change in the pixel value, defined earlier, of
the viewed image to start recording the video. This function is important for, exactly, defining a frame of reference for comparing the recorded videos of the electrified drops. It is also important when analyzing the videos for the response time measurements.

The DSA software relies on the contour lines of the produced images to perform contact angle measurements. Therefore, it is important to setup the images with the highest possible resolution (definition in this context). An image of a fitted drop is presented in Figure 3.12. The drawback of the CCD camera that the DSA is equipped with is the relatively low frame rate. The maximum recording ability of the CCD camera with a resolution of $780 \times 580$ is 62 frames per seconds (fps). This resolution is the best resolution for observing the studied phenomena. This is a limitation, which can be overcome by using a high-speed camera.
Figure 3.12 A fitted drop as it appears in the DSA screen system. The blue line represents the base line of the drop. The base line of the drop can be identified from the reflection of the drop on the surface. The green line represents the best-fitted line around the drop outer surface. Contact angle and drop dimensions calculations are based on these two distinct lines.

3.5.2 High-speed camera

The high-speed camera is a useful tool for observing the fast occurring phenomena. The system is capable of recording videos of the electrified drops at a very high frame rate. For most cases, 500 fps recording speed was used at the highest resolution. The camera was used, in occasions, at higher frame rates with lower resolution (image size). As the frame rate increases, more requirements are needed to be able to acquire acceptable quality images. It was determined that in most cases 500 fps imaging speed is sufficient for analyzing the observed phenomena in this study.
Because electrocoalescence and drop movement on coated surfaces occur in high speeds, the high-speed camera was used to obtain images of these phenomena. The trade-off of using the high-speed camera was the fact that the images were not having high quality to be able to conduct the contact angle measurements in often times. In some cases, though, the images produced by the high-speed camera were in good quality for obtaining certain dimension measurements. In some occasions, both the high-speed camera and the CCD camera were used simultaneously to obtain the images of the electrified drops in one experimental setup. One camera captures the images of the drops for a side view and the other camera capture the images of the drops for the top view. For example, in one experimental setup both cameras were used as shown in Figure 3.13.

Figure 3.13 Experimental setup for producing images of the observed drops. The images are produced simultaneously and independently by two camera systems. The CCD camera produce high quality images for contact angle measurements, while, the high-speed camera produce acceptable quality images of the fast occurring phenomena.
Both camera systems complimentary served for observing the electrified drops. It will be indicated in each relevant experiment the kind of camera used for observing the drops and the frame rate used. It will also be indicated the reasoning behind using the specific type of camera. It is worth mentioning that both camera systems were used for producing top and side views of the observed drops with some modifications. The CCD camera was fixed on the DSA frame and a beam splitter was used to further increase the imaging capabilities of the CCD camera. On the other hand, the high-speed camera was mounted on a free rotating axis enabling easier maneuver.

3.6 Surface properties measurements

Surface tension of the polymeric solutions was an important parameter in many experimental investigations. Surface tension measurement techniques vary depending on the liquid physical properties and quantity. The DAS was used for measuring the surface tension of the polymeric solutions in many occasions. However, in some circumstances other equipment were used for characterizing the surface tension of the polymeric solutions. In some cases, there were modifications to the characterizing procedures usually followed for obtaining the surface tension with DSA.

Contact angles were measured using the DSA automated software, when the images were produced using DSA. In other occasions, when the images were produced using other imaging equipment, then image J software was used.
The contact angle measurements using image j relies on the quality of the images, in addition to other factors. For instance, contact angle measurements using image j can be conducted using different functions. In this work a plug-in was used to measure the contact angle using image j.

3.7 Coating techniques

In all studied phenomena, the coating technique was a crucial step in forming the coatings. There are many methods for coating different shapes and geometries of substrates. The techniques that were chosen for conducting this research project were spin coating and dip coating techniques. Each technique had advantages over the other one. These techniques are discussed in details in the following sections. Each one was used for specific purpose. The advantages and disadvantages will also be demonstrated.

3.7.1 Spin coating technique

Spin coating was used, mainly, for flat surfaces to produce a uniform coating whenever was desired. In spin coating the thickness of the coating depends on many parameters. Viscosity, surface tension, temperature, surface properties of the substrates could have effects on the uniformity of the coating. More importantly, the spinning speed definitely affects the thickness of the coating. In this research endeavor, the spinning speed was fixed to be 1500 revolution per minute (rpm). The reason was due to the fact that the comparison of the coatings was based on the dissolved polymer concentration as a control
parameter. The concentration of the dissolved polymer affected the solution properties as well be presented in chapter IV. The concentration variation was the control parameter that was of interest. Figure 3.14 shows an image of the spin coater with the essential parts for operating it.

![Spin Coating Setup](image)

Figure 3.14 Spin coating setup. The spin coater can be used to coat flat geometry substrates. The spin coater can be programmed for spinning at different speeds and accelerations as desired. It was used for coating flat substrates at a fixed rpm of 1500. The programming keypad enables the user to define a spinning speed and duration.

### 3.7.2 Dip coating technique

Dip coating technique was used for coating different kinds of substrates. The advantage of using this technique is the ability of coating different geometries. The dipping speed can have a great effect on the uniformity of the applied coating. A custom-made dip coater was built to accomplish the task of coating rectangular substrates as well as cylindrical substrates. The dip coater
consists of a motor with a spool attached to it. As the spool rotates, the wire attached to the spool moves in the vertical direction guided by two pulleys. A clamp attached to the free-dangling wire allows for sample mounting. The direction of the vertical movement can be controlled using a three-way switch. The three-way switch allows for reversing the polarity of the supplied DC voltage to the motor. Using the three-way switch, the sample can be dipped-in and dipped-out of the solution. The dip coater was modified for better control over the vertical direction by adding a rail and glide for guiding the clamp that was attached to the end of the free-dangling wire. An image of the custom-made dip coater is given in Figure 3.15.
Figure 3.15 The custom-made dip coater consists of a motor that rotates the attached spool. A wire is wrapped around the spool and guided by two pulleys for moving the sample upwards and downward. Varying the supplied voltage to the motor can control the speed of dipping. By using the reversing polarity switch, the direction of the vertical movement can be precisely controlled. The dipping, takes place inside an isolated environment with the help of a transparent front cover to minimize sample contaminations.

Varying the DC voltage that powers the motor controls the speed of dipping. Often times, the voltage that powers the motor was fixed at a specific value to give a specific dipping speed. However, the power supply was replaced with the programmable power supply to have the ability of varying the dipping speed while dipping the sample. More details about the programmed dipping will be discussed in Chapters IV and VI. Figure 3.16 shows the dipping speed for different voltages. The range at which there is correlation between the powering voltage and the dipping speed was 3 to 12 VDC corresponding to 0.128 to 0.832 ± 0.001mm/s.
Figure 3.16 First order linear regression was used to obtain the correlation between the powering voltage and the dipping speed. The data were collected for each voltage in triplicates for both upwards and downwards vertical directions. The $R^2$ value shows the goodness of fit for the fitted data. The tolerance for the set speed is 0.001 mm/s.

From the graph above, as the powering voltage that was used for running the motor increases, the dipping speed increases. There was a strong correlation in this voltage range between the powering voltage and the dipping speed. The correlation is given by

\[
\text{Dipping speed} = 0.0779 \times \text{Powering voltage} - 0.1002
\]

This correlation was used for the variable speed dipping. In other words, when the programmable power supply was used to power the motor, the powering voltage was programmed to change over a period of time resulting in a change in the dipping speed. The change in dipping speed can be found from the above correlation whenever was needed.
Spin coating and dip coating were the coating techniques used for applying the coating in all cases presented in this thesis. It will be indicated whenever is appropriate which technique and what program was used for each experimental investigation.

3.8 Drop size distribution characterization

Most commonly method of characterizing the filter performance is by analyzing drop size distribution in a given sample. Comparing the drop size distribution of different samples helps understanding the performance of the challenged filter media. There are many equipment that can perform the sizing of the particles in samples. Depending on many parameters, one can choose specific equipment for characterizing a given sample. In this research project, the interest was on characterizing the distribution of water droplets present in diesel emulsions. There were two equipment that were used for carrying the drops size distribution investigations.

3.8.1 Particle Sizing System (Accusizer)

Accusizer was used for generating the drop size distribution of two phases dispersion samples. It relies on the differences of the refractive indices of the phases of the sample constituents. Water droplets dispersed in diesel are spherical in shape, when they pass through the detection channel; they interact with the laser beams inside the channel. The software calculates the diffraction of
the laser beams, and based on that a drop size distribution is generated. Figure 3.17 shows the main components of the Accusizer system. The detector that was used can detect particle sizes ranging from 0.5 to 500 μm.

Figure 3.17 Accusizer particle counter. The sample to be analyzed should be in a beaker with a known volume. The sample is put inside the sample stage champer. Through pressurized air, portion of the sample is sucked and passes through the detector channel for drop size analysis. When the analysis is done, the analyzed sample is sent to the effluent liquid storage tower, which can be properly disposed of afterwards. The data processing box, receives the signal from the detector that is mounted on the sample stage champer and processes the signal and sends the data to the computer for further processing. The software in the computer reports the particle size distribution of the analyzed sample.

The Accusizer was a tool that was available for measuring the drop size distribution of the studied dispersions. The drawback of using the Accusizer for analyzing the sample was the fact that it analyzes discreet samples. This may have effects on the accuracy of the drop size distributions as time progresses. From the moment of collecting the dispersion sample to the moment of analyzing the sample, there is a time lag that may affect the precision of the analyzed...
sample. It was then determined that another characterizing technique is preferred for comparing the outcomes from both equipment. The second method depends on imaging the flowing dispersion.

3.8.2 Visual Process Analyzer (Jorin ViPA)

The Jorin ViPA system is a tool that was available for measuring the particle size distribution in a continuous sampling mode. The system depends on a relatively high-speed imaging method for generating the drop size distribution. The speed of imaging is 100 frames per second (fps). The dispersion flows through the instrument, passing through a thin channel where imaging window is located. The camera captures images at 100 fps at a fixed depth of field. At this depth of field, the images are focused, enabling the software to distinguish between different phases. Figure 3.18 shows the particle counter system, Jorin.

![Jorin ViPA system](image)

Figure 3.18 Jorin ViPA system. This system is in-line characterization technique. The dispersion is continuously evaluated as it passes through the imaging window. A steady flow rate has to be maintained to obtain sustainable results. The flow rate requirement is in the range of 40 to 60 ml/min.
Jorin ViPA system is a helpful tool in analyzing the samples in continuous mode. However, the disadvantage of this system is the fact that a certain flow condition must be sustained. It was not always possible to achieve these requirements. The other disadvantage is the limitation arises from fixing the sampling point. For example, one can only analyze the inlet or the outlet of the coalescing device in an experimental trial. There is no way of obtaining the drop size distribution of the inlet and outlet (from and to) the coalescer in an experimental trial. An option of diverting the flow through fitting loop alternatively was considered. However, the perturbation of the flow through the fitting was a concern and thus the modification was excluded.

3.9 Concluding remark

In this chapter, the experimental setups that were essential for conducting the research investigations were briefly demonstrated. Purchased equipment that were primarily used, were also demonstrated. In addition, customized equipment was demonstrated with its working principal. The operation of all equipment presented in this chapter was briefly explained. Complementary materials are given in Appendices.
CHAPTER IV

COATING, CHARACTERIZATION AND PATTERNING

4.1 Introduction

Applying coatings to substrates is a crucial step for surface modification practices. Many methods can be used, some of which are complicated, while others are relatively simple. Advanced methods such as Chemical Vapor Deposition (CVD) (179, 180), Physical Vapor Deposition (PVD) (181, 182) require advanced equipment and time consuming procedures. In contrast, spin coating and dip coating techniques are relatively simple. Spin coating and dip coating methods are adapted in this work for their simplicity and effectiveness.

4.1.1 Chapter overview

This chapter discusses three major topics. The first topic, talks about the solution preparation protocols and solutions physical properties. The second topic provides details about the coating methodologies and characterization. The last topic is devoted towards coating patterning techniques investigations.
4.2 Solutions preparations

Different polymeric solutions were used in this research project. All solutions were prepared consisting of two main constituents, a solvent and a solute. The solvent was Toluene and the solute was poly (styrene-co-methyl methacrylate) copolymer with molecular weight 100,000-150,000, 40% styrene. This polymeric blend was used as the dielectric protective layer in electrowetting experiments. The concentration of the polymer was varied for different purposes. The concentrations of the polymer by weight were 5%, 10%, 15%, 20%, 25%, 30% and 35%. Each solution was characterized independently and following the same standards. The physical properties that were of interest were density, surface tension, and dynamic viscosity. For all solutions, a mechanical shaker mixer was used at 200 rpm and 25 °C mixing conditions. It was found that as the concentration of the polymer increased, more time was needed to achieve complete dissolution. The time required for achieving complete mixing for the concentrations 20% and above was 4 days.

4.2.1 Physical properties of solutions

Densities of the polymeric solutions were measured using the standard methods for measuring density. Briefly, 5 ml of the solution was dispensed using a micropipette (with the proper pipette) into a small vial on a microbalance. From the volume and mass of the samples, the density was calculated. The measurements were done in triplicate and the uncertainty of the measurements was taken into account. Figure 4.1 represents the density of the polymeric
solutions as a function of the concentration of the polymer. The measurements were conducted in triplicates using the standard density measurements techniques.

![Graph](image.png)

**Figure 4.1.** Density of the polymeric solutions measured at 25 °C. As the concentration of the polymer increases, so does the density of the solution. The error bars represent the range of the calculated densities demonstrating the accuracy of each measurement.

Density measurement was important for surface tension measurements. The surface tension measurements were conducted by two methods. The first method was by using the Drop Shape Analyzer (DSA20E, Krüss GmbH, Germany) demonstrated earlier in Chapter III. The second method was by using a Tensiometer (DuNouy Tensiometers, CSC Scientific Company INC. Fairfax, VA). For the first method, the surface tension measurements were conducted by using the pendent drop method by the DSA. The DSA implements an analytical-image processing algorithm to calculate the surface tension of a pendant drop. The analytical-image processing method requires the knowledge of the density of
the liquid in question. The shape of the pendent drop is the most important parameter in calculating the surface tension. In the second method for obtaining surface tension, though, the density measurements were not needed. The surface tension measurements were conducted in triplicates in both methods. The values obtained from both techniques were in close proximity, confirming the validity of the measurements. The surface tension values were averaged and are shown in Figure 4.2.

![Surface tension graph](image)

Figure 4.2 Surface tension of the polymeric solutions as a function of the polymer concentration, measured at 25 °C. The reported values are the averages of six data points at each concentration. Three data points from the DSA measurements and three data points from the Tensiometer measurements. The error bars represent the ranges of the measurements.

Dynamic viscosity of the solutions was measured by using two techniques. The first technique was by using a Brookfield Dial Viscometer (Brookfield Engineering Laboratories, INC. Middleboro, MA). Large volumes were needed to
conduct the viscosity measurements by using this rheometer. It was used for the low concentration solutions. The second technique was by using a rheometer. This rheometer required small volumes for obtaining the viscosity of the solution, which was an advantage. Figure 4.3 shows the dependency of viscosity of the solution on the polymer concentration. The relationship is not linear, but rather an exponential relationship.

![Figure 4.3 Viscosity of the polymeric solution as a function of the polymer concentration. The viscosity increases exponentially as the polymer concentration increased.](image)

Polymer concentration had great effects on the solution properties. These variations, in turn, had effects on the deposited films thicknesses. Thickness and uniformity of the coating strongly depended on the polymer concentration. In the next section, investigation results of different coatings are presented.
4.3 Coating techniques

The coating was conducted using spin coating and dip coating. Both techniques were used for preparing surfaces in electrowetting experiments. The methods used for applying the coatings using spin coating will be discussed in the following section. After that, the techniques used in dip coating will be demonstrated in the subsequent section.

4.3.1 Polymeric films by spin coating

The spin coater was used for coating flat surfaces. The substrates used in these investigations were glass slides. The glass slides were cut into 2 by 3 cm rectangles. The glass slides were cleaned using soap and water. After that, they were rinsed with tap water. Then, they were rinsed with ethanol/water mixture (10%/20% by volume). The final step was drying with lint-free napkins. That was the protocol for cleaning the surfaces.

All glass rectangles were coated with the polymeric solutions at a set speed of 1500 rpm. It is well known that the spinning speed has effects on the uniformity and thickness of the formed films. However, the goal was to investigate the effects of the polymer concentration on the thickness of the films. Figure 4.4 shows the thickness of the coatings as a function of the polymer concentration. The thicknesses were measured using a Profilometer (Dektak 150 surface profiler, Veeco Instruments Inc.).
Figure 4.4 Spin coated film thickness as a function of the polymer concentration only. The spinning speed was set at 1500 rpm for all coated substrates. There is a relationship between the polymer concentration and the film thickness. The measurements were done by a Profilometer in triplicates. The error bars are not visible in the graph due to the fact that the equipment has high resolution.

From Figure 4.4, there is an exponential relationship between the film thickness and the polymer concentration. This correlation between the film thickness and the polymer concentration was also observed with the measured viscosity of the solutions. This dependency of the film thickness on the viscosity is, in a sense, not surprising.

4.3.2 Polymeric films by dip coating

The dip coater demonstrated previously in chapter III was used for coating the substrates. The substrates in this investigation were glass slides prepared the same way explained in the previous section. The dimensions and the cleaning procedures were the same as described earlier in the previous section. The dipping protocol was the same for the upward and downward vertical
direction. For all surfaces, the dipping speed was 0.80 mm/s. First, the substrates were dipped inside the solution at this constant speed. Once two-thirds of the substrate was submerged in the solution, the direction of the dipping was reversed to the upward direction at the same speed. A schematic of the custom-made dip coater is shown in Figure 4.5.

**Figure 4.5 Dip coating setup.** This setup was described in chapter III. The dipping in this investigation was done using a constant speed of 0.80 mm/s for all substrates.

The dipping was done in controlled environmental temperature of 22.5 ± 0.5 °C. The varied parameter was the concentration of the polymer used for each substrate. The previously described polymeric solutions were used for this investigation. The purpose of this investigation was focused on the uniformity of the coating. It was speculated that there was a gradient coating forming on the
substrate caused by dip-coating technique. The procedure was done for all substrates the same way. A portion of the substrate was selected for investigating the gradient on that specific portion. Due to equipment limitations, the scanned length was limited to 500 $\mu$m. The 500 $\mu$m location on the glass slides was about 2 mm from one end of the coated area. This was set to avoid the end effects of the coating on the slides and to account only for the gradient of the coating. A schematic of a hypothetical slide is shown in Figure 4.6.

![Figure 4.6 A schematic of a hypothetical slide. The gray area represents the coated portion of the glass slide. The sketch is not to scale, and the dimensions unit is millimeter. The scanned area was varied but far from coated edges. The width of the slide is 20 mm.](image)

The gradient in the scanned portions of the slide was measured three times using the Profilometer. The location of the scanned area was also varied for these measurements. The locations of the new scanned areas were far enough from the edges of the coated portion. The gradient is represented in Figure 4.7.
From Figure 4.7, the gradient was somewhat dependent on the solution concentration. However, there were reservations on the ability of the equipment to quantify the gradient precisely. Ideally, the whole coated portion of the slide should have been examined. This approach was investigated, however, the results were misleading. After analyzing the results, the conclusion based on this study was to exclude the idea of scanning the whole coating. The equipment has a very high resolution and is very sensitive. The slides are not ideal and it was speculated that a tiny tilt angle of the slide on the examination stage might gave rise to these contradicting results. Hence, the gradient results in this set of experiments were considered unreliable and were not used in any kind of calculation.
The conclusions that were drawn from these tests was that the coatings were not uniform and there was some kind of gradient on them. Extensive efforts were devoted to find other ways of precisely quantifying the gradient. However, these were the best achievable results within the limited time and resources that were available.

In this set of experiments, the gradient was believed to form due to the dipping technique that was used. Despite the fact that efforts on precisely quantifying the gradient were not very successful in obtaining a meaningful conclusion, these results inspired another design of experiments. The gradient developed by the new experiments was precisely controlled and measured. The new designed experiments are discussed in Chapter VI, in the drop movement experiments. In addition, a new dipping protocol is discussed in section 4.4.

4.4 Coating morphology (patternning)

It is well known that the surface topology has effects on the contact angle, and hence the wettability. As a result, the wettability behavior of a material can be modified by altering the surface topology. Changing the morphological structure of a surface can be achieved by many different methods. Some methods more complicated compared to others. For example, photolithography is a technique that can be used to form different structural features of a coating on a surface. Photolithography is a very useful technique and can be used to precisely control surface features. However, it is considered a complicated and
time consuming process (183). Photolithography is often times used for surface patterning (184). There are many other methods, but they are beyond the scope of this discussion.

Nemours analyses were conducted to study the effects of patterned coatings on wettability(185–187). Surface patterning is common way of altering the wettability behavior of a material. Surface patterning is very useful in many other applications, too. For example, patterned micro channels were used in producing mono dispersions(188). In optics, pattered surfaces are sometimes desirable in light diffraction applications (189).

4.4.1 New paradigm

The results from the previously shown coating's investigations have lead to designing a new dipping protocol. This new protocol was the control parameter responsible for fabricating patterned coatings. Reproducibility was investigated, and results showed very consistent outcomes. Briefly, the new dipping protocol produced cosine-like structured layers. Experiments and results will be shown next.

4.4.2 Dipping protocol description

The coating was applied into the substrates in stage wise sequences. The key to form the pattern was to pull the sample from the solution after the submerging stage, periodically. The time between each period was 60 seconds.
First, the sample has to be submerged into the solution. Next, the programmable power supply powers the motor to withdraw the sample from the solution. The withdrawal is not continuous, but rather in stages. There were two programs for the withdrawal sequence. The first program was to withdraw the sample from the solution for 1.0 second followed by 60 seconds pause period. Then, the cycle repeats until the whole substrate is coated. The second program was to withdraw the sample from the solution for 0.5 second followed by 60 seconds pause period. After that, the cycle repeats until the whole substrate is coated. Figure 4.8 shows a graphical representation of the withdrawal sequence for 9 periods, as an example.

![Graphical Representation](image)

**Figure 4.8** Nine withdrawal periods. These periods are for the withdrawal stage. The sample is pulled at a constant speed for a short period of time (either 1.0 or 0.5 second) followed by 60 seconds halt period.
As mentioned above, the withdrawal periods are either 1.0 or 0.5 second. The withdrawal periods are represented graphically in Figure 4.9. These sequences were programmed using the programmable power supply. The voltage that powers the motor in the dipping setup was controlled by the programmable power supply. Hence, the rotation of the motor at every moment in time was controlled. Using the data acquisition system described in Chapter III, the data points for these graphs were collected.

![Graphical representation of withdrawal cycle](image)

Figure 4.9 A graphical representation of one withdrawal cycle. The graphs show the speed and duration for each program.

4.4.3 Patterned coating results

The 1.0 and 0.5 second programs were used for the polymer concentrations 10%, 20%, and 30%. This gave a total of six different pattern structures. The patterns have a cosine-like structure. Each pattern has a distinctive wavelength and amplitude associated with it. Depending on the polymer concentration and the program used for the withdrawal sequence, the patterned coating forms. Figure 4.10 shows optical images of different pattern
structures. The illumination technique was different for each slide. The reason was due to the fact that each pattern was refracting light in different manner depending on its morphology.

Figure 4.10 Six different patterns on six glass slides. The pattern structure depended on the polymer concentration and the program used, as well.

The patterned coatings were transparent. This made it very challenging to take images of the patterned coatings. The images were produced by using Olympus (SZ 61) polarizing microscope. Moreover, the images were produced using different illumination techniques. This is due to the fact that each pattern has different optical and morphological properties. The topology was investigated by using the Profilometer that was previously used for coating thickness characterization. Figure 4.11 shows the results obtained by using the Profilometer.
Figure 4.11 Six different patterns with different amplitude and wavelength. Note the vertical axis scale for the 30% polymer concentration. The 30% polymer concentration for both programs gave very small amplitudes compared to the other patterns.

By inspecting the images and the results from the Profilometer, it is clear that each coating has distinct features. The wavelength (node to node horizontal distance) and the amplitude (in our case is the total vertical distance) values are tabulated in Table 4.1 with the ranges for each coating pattern.
Table 4.1 Characteristic dimension of the patterned coatings.

<table>
<thead>
<tr>
<th>Program</th>
<th>Wavelength ($\mu m$)</th>
<th>Amplitude ($\mu m$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% (1.0 second) program</td>
<td>630 ± 22</td>
<td>0.87 ± 0.09</td>
</tr>
<tr>
<td>20% (1.0 second) program</td>
<td>680 ± 38</td>
<td>0.5 ± 0.14</td>
</tr>
<tr>
<td>30% (1.0 second) program</td>
<td>682 ± 17</td>
<td>0.09 ± 0.02</td>
</tr>
<tr>
<td>10% (0.5 second) program</td>
<td>273 ± 7</td>
<td>0.37 ± 0.06</td>
</tr>
<tr>
<td>20% (0.5 second) program</td>
<td>130 ± 26</td>
<td>0.08 ± 0.01</td>
</tr>
<tr>
<td>30% (0.5 second) program</td>
<td>142 ± 7</td>
<td>0.003 ± 0.0006</td>
</tr>
</tbody>
</table>

4.4.4 Results analysis and interpretation

It is believed that the patterns form due to two competing forces. The first one is the gravitational force and the second one is surface tension force. Evaporation of the wetting liquid plays an important role in the pattern formation. In both programs, the halt period was 60 seconds. This halt period was obtained by trial and error. It was found that during this 60-second halt period, a solid film forms at the liquid/solid interface.

After pulling the substrate from the solution, the surface is wetted by the solution. There are many factors affecting the film formation. For example, the free surface of the solution is making a contact angle with the wetted surface. This combination of contact angle and polymer concentration affects the evaporation at the liquid meniscus. Viscosity and surface tension change by varying the concentration of the polymer. These changes affect the free surface
flow at the substrate/solution interface. All these variations can have effects on the deposited films on the substrates. However, these effects were not investigated in this work.

In fact, one can predict how the film pattern forms based on the physical properties of the solution with the basic knowledge of free surface flow phenomena. In this research endeavor, though, no attempts were given to investigate on the film formation. These results on coating patterning were obtained in the final stages of this research project. Suggestions will be given in Chapter IX for future work.

4.5 Concluding remarks

All these investigations on the coatings were conducted for the dielectric film. The hydrophobic film (FluoroPel) thickness was investigated and was found to be 50 nanometers. The thickness of the hydrophobic film was investigated on a glass slide using ellipsometry.

Coating thickness investigations allowed for the calculations of the theoretical contact angles predicted by Young-Lippmann equation. In the following Chapter, discussion on the contact angle changes as well as electrowetting phenomena will be presented.
5.1 Introduction

Electrowetting and electrocoalescence phenomena in air media were investigated. Vertical electrode, horizontal electrode, and parallel flat slides electrodes were used to study these phenomena. The description of these electrode arrangements was given in Chapter III. In this chapter, electrowetting and electrocoalescence phenomena in air media investigations will be presented.

5.1.1 Chapter outlook

This chapter is organized into the following:

- Section 5.2. Includes time-image synchronization description.
- Section 5.3. Presents electrowetting study in the vertical electrode arrangement for spin-coated films on ITO slides.
- Section 5.4. Discusses electrode orientation effects on contact angle modulation on stainless steel substrates.
Section 5.5. Demonstrates electrocoalescence study in the horizontal electrode arrangement for dip-coated films on ITO and stainless steel substrates.

Section 5.6. Presents electrocoalescence study in the parallel electrode arrangement for dip-coated films on stainless steel substrates.

Section 5.7. Conclusion.

5.2 Timing and image synchronization layout

The experimental setups for electrowetting experiments were demonstrated earlier in Chapter III. All setups can be used with this imaging platform. The imaging platform is shown in Figure 5.1.

Figure 5.1. A general layout for accurately synchronizing images with time. The setup was used for electrowetting, drop movement, and electrocoalescence experiments. The description and the operation of the system are given in the text.
The output voltage was programmed for different electrowetting experiments. Each program was saved and acquired whenever needed. Once a specific investigation was needed, the saved programmed sequence was executed. When triggering the system, images of the electrified drops are saved in the computer, and the voltage profile is saved in the computer, too. The images of the electrified drops can be acquired for further analysis.

The function of the programmable power supply outputs was explained in Chapter III. Figure 5.2 shows a flow chart for the data synchronization method. Briefly, by executing the saved sequence a number of events start simultaneously. This allows for identifying a reference time when analyzing the images on a timely basis.

Figure 5.2. Flow chart of the image-time synchronization process in the imaging platform.
5.3 Vertical electrode arrangement for spin coated films

Contact angle change was studied for the vertical electrode arrangement for 5%, 10%, 15%, 20%, 25%, 30%, and 35% polymer concentration spin-coated films. These different concentrations were used of the dielectric film layer. The hydrophobic layer was as always FluoroPel coated on top of the dielectric layer. Solution preparation and characterization was demonstrated in Chapter IV. The substrates used in this investigation were ITO glass slides. The vertical wire used was a copper wire, 128 $\mu$m diameter. The experimental setup was described in Chapter III. The discrete phase was deionized water droplet with electrical conductivity 0.40 to 1.12 $\mu$S/cm. The continuous phase was air.

5.3.1 Objectives

This investigation was conducted to characterize contact angle change due to the applied voltage. The purpose was to monitor contact angle change with the applied voltage on a timely bases. This monitoring was not seen in the reviewed literature. In the reviewed literate, the contact angle changes were reported for discreet points with the applied voltages. Unlike the approach that is usually followed, the contact angle was monitored on time and voltage bases. This investigation was conducted for spin-coated films on ITO glass slide. The vertical wire electrode was used in this study.
5.3.2 Results and discussion

Voltage was applied to drops sitting on spin-coated films on ITO glass slides. As it was seen in Chapter IV, the film thickness depended on the polymer concentration. Hence, the voltage range was varied according to the film thickness. By rigorous experimentations, the threshold voltage value for each thickness was identified. After that, a voltage bias for a short exposure time was applied to the drops. Hence, a change in contact angle can be observed and quantified. Table 5.1 shows the saturation voltage and short exposure time for each polymer concentration. The saturation voltage was identified from other experiments. The saturation voltage is defined as the maximum voltage that contributes to a stable change in contact angle. The table also shows other details. Both the short exposure time and the recording time were determined from previous investigation based on the electrified droplets performance. Each thickness has a different electrowetting performance. Thus, a different program was designed to test electrowetting effect on each thickness independently.
Table 5.1. Voltage bias for spin-coated films based on polymer concentration used in spin coating. Recorded videos durations are also given. Imaging speed was 62 frames per second.

<table>
<thead>
<tr>
<th>% Polymer</th>
<th>Saturation voltage (VDC)</th>
<th>Exposure time (sec)</th>
<th>Recording time (sec)</th>
<th>Recorded images</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>100</td>
<td>3</td>
<td>8</td>
<td>496</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>3</td>
<td>12</td>
<td>744</td>
</tr>
<tr>
<td>15</td>
<td>150</td>
<td>3</td>
<td>12</td>
<td>744</td>
</tr>
<tr>
<td>20</td>
<td>250</td>
<td>3</td>
<td>12</td>
<td>744</td>
</tr>
<tr>
<td>25</td>
<td>300</td>
<td>3</td>
<td>12</td>
<td>744</td>
</tr>
<tr>
<td>30</td>
<td>450</td>
<td>6</td>
<td>16</td>
<td>992</td>
</tr>
<tr>
<td>35</td>
<td>550</td>
<td>8</td>
<td>20</td>
<td>1240</td>
</tr>
</tbody>
</table>

The CCD camera starts recording as soon as the voltage is applied to the droplets. A white spot on the droplet indicates that the voltage either ramping up or ramping down, as a visual indication. The voltage ramp is acquired by the data acquisition system and plotted in the same time. Figure 5.3 shows the change in contact angle as a function of voltage and time, for the 5 % as a demonstration. Contact angle measurements were done automatically for all images by the DSA software. Contact angle change as a function of voltage and time were plotted for all seven thicknesses. For each slide, the experiment was conducted twice. The error bars are included in each plot and they represent one standard deviation for the averaged contact angles along the contact angle curves.
Figure 5.3. Selected images from a video sequence. The films were 5% polymer concentration spin coated on ITO glass slides. The bias voltage was 100 VDC. Notice the small bright spot indicated by the arrows in each image. The bright spot is the reflection from the LED light, which was used to trigger the camera recording function. The camera starts recording automatically for 8 seconds then it stops recording. When that spot appears in the image, it indicates that the voltage at that moment in time was above zero VDC.
The sequence in Figure 5.3 shows the change in the shape and contact angle of the electrified drop on the 5% polymer concentration spin coated on ITO glass slide. From the videos described in Table 5.1, the contact angle for all coated surfaces was measured as a function of voltage and time. Figure 5.4 shows electrowetting performance on all spin-coated films.
15% Polymer concentration spin coated film

20% Polymer concentration spin coated film

25% Polymer concentration spin coated film
Figure 5.4. Contact angle change of 5 microliter water droplets sitting on spin coated surfaces with different polymer concentrations. Voltage exposure time was varied for different substrates according to the dielectric strength of each thickness.

From Figure 5.4, as the concentration of the polymer increases, so does the saturation voltage. Also, at the saturation voltage contact angle hysteresis is notable for all tested films. In addition, by examining the plots one can see that the change in contact angle follows the same trend as the voltage rampage used.
The voltage rampage is an equipment limitation as described earlier in Chapter III. Nonetheless, it gave information about the contact angle modulation as a function of voltage slew rate. The slew rate was affecting the change in contact angle as shown by the curves.

The gap distance between the bottom part of the vertical wire electrode and the coated surface was $800 \pm 50 \mu m$ in all cases in this study. The objective of this study was not focused on the effects of the gap distance on contact angle change. Rather, it was focused on the effects of the film thickness on the contact angle modulation. The electrode geometry and orientation has effects on the contact angle, and this is discussed in the following section.

5.4 Electrode orientation effects on contact angle modulation

In this study, dip coated films were used. Only one polymer concentration for the dielectric layer was used in this study. In addition, the composition of the dielectric layer solution was slightly modified. The solution consisted of 10% by mass poly (styrene-co-methyl methacrylate), 80% Toluene, and 10% Krytox solvent (DuPont, Wilmington, DE, USA). The dipping speed was 0.80 mm/s. This investigation was carried out using the vertical and horizontal electrode arrangement with coated stainless steel substrates. The hydrophobic layer was FluoroPel™. The wire electrode was the same copper wire used for all investigations.
5.4.1 Objectives

The objectives were to:

- Evaluate contact angle hysteresis of water drops on the coated stainless steel plates by using advancing/receding method and drop evaporation method.
- Establish a frame of reference for applying the voltages to the drops.
- Evaluate contact angle electro-hysteresis of water drops, caused by applying voltage to water drops in electrowetting configurations by using short and long time exposures tests.
- Evaluate the effects of the electrode orientation on contact angle.
- Compare the experimental contact angles to the predicted contact angles.

5.4.2 Inherent hysteresis evaluation

The objective of conducting contact angle hysteresis study was to establish a reference time for applying voltage. This reference time can be referred to for electrowetting experiments. This will minimize the discrepancies in initial contact angle before applying the voltages and allows for fair comparisons. This method insures that the initial contact angle falls within a specific range dictated by the surface properties of the coated surfaces.
The inherent hysteresis was evaluated by using two methods. The first method was the advancing/receding method. This method depends on measuring the contact angle of the drop while either increasing or decreasing its volume. A 5-microliter drop was first dispensed on the surface. After that, using an automated micro drops dispenser, the volume was changed. The change in volume has to be slow enough so that the change in contact angle is a function of the surface properties only. 10 microliter/ min is an appropriate rate for the drop volume change in this experiment. The advancing contact angle is the one measured while the volume increases. The receding contact angle is measured while the drop volume decreases. The difference between the maximum advancing contact angle and the minimum receding contact angle is the inherent hysteresis.

The second method is the drop evaporation method. This method evaluates the change in contact angle of the drop for 15 minutes as the liquid in the drop evaporates. First, the drop is dispensed on the coated surface. The drop is video recorded for 15 minutes as the droplet evaporates. The drop evaporates and the contact angle changes due to evaporation. The hysteresis in the drop evaporation method is the difference between the maximum contact angle and the minimum contact angle during evaporation.
In the advancing/receding test, a five-microliter droplet was dispensed on the coated stainless steel plates. By using the syringe the volume was increased. Finally, the added volume was drawn from the drop at the same rate of 10 microliter/min. Figure 5.5 shows the advancing and receding contact angles.

![Figure 5.5](image.png)

Figure 5.5. Advancing and receding contact angle measured on the coated stainless steel plates for inherent contact angle hysteresis. The dispensed droplet volume was 5 microliter. The volume of the droplet was increased to approximately 20 microliter in the advancing stage. Finally, it was reduced to roughly 7.5 microliter for the receding stage. The hysteresis is 24°. The data represents two experimental trials. The error bars are for one standard deviation. The instrumental error is 3%.

Figure 5.5 represents the contact angle as a function of time. The oscillation in the advancing stage might be due to surface roughness. This oscillation is not noticeable in the receding stage beyond roughly 100 seconds. This is due to the fact that the liquid wetted the surface in the advancing stage. Consequently, in the receding stage there was less perturbation in the receding
contact angle of the wetted surface. From Figure 5.5 the hysteresis was calculated and found to be 24° (difference between maximum advancing angle and minimum receding angle).

In the drop evaporation method, a five-microliter drop was dispensed on the coated surface and left to evaporate for 15 minutes. The temperature of the surrounding air was 25.5 ± 2 °C. The drop reduced in volume from 5 ± 0.15 microliter to 2 ± 0.27 microliters. Figure 5.6 shows the contact angle and volume reduction rate during the 15-minute test.

Figure 5.6. Drop evaporation method for inherent contact angle hysteresis investigation. The data represent three experimental trials. The instrumental error is 3%. Error bars represent one standard deviation for each averaged contact angle at each moment in time. The hysteresis in this case is 10°.
The hysteresis from Figure 5.6 was calculated and found to be 10° (difference between maximum angle and minimum angle). Also, from Figure 5.6, the contact angle oscillated dramatically after about 400 seconds of dispensing the drop. This is due to the change in the length of the base diameter of the drop. The base diameter decreased due to evaporation. There were big variations in the base diameter as shown in Figure 5.7. This might be due to surface topology variations, which affects the adhesion of water molecules to the coated surface and thus contact angle.

![Figure 5.7. Drop base diameter. The base diameter was obtained by the DSA at each second during the test. There were large variations in the base diameter beyond roughly 400 seconds. As the droplet got smaller in size and the contact angle oscillated after 400 seconds corresponding to the oscillations observed in Figure 5.6.](image)

The hysteresis from the advancing/receding method was found to be 24° (difference between maximum angle and minimum angle). While, it was found to be 10° (difference between maximum angle and minimum angle) from the drop
evaporation method. There is a big difference in hysteresis obtained by the two methods. A plausible explanation is that in the advancing/receding method, the drop volume was much larger than in the evaporating drop method. The implication of this is that the contact angle encounters more perturbation by larger area in the advancing/receding method than in the drop evaporation method. These perturbations were caused by different degrees of variations of surface morphology. In addition, the drop evaporation method depended up on the receding contact line through drop evaporation. The receding contact line was moving very slowly during evaporation. The hysteresis results from the advancing/receding and the drop evaporation methods are summarized in Table 5.2.

Table 5.2. Summary of hysteresis results

<table>
<thead>
<tr>
<th>Method</th>
<th>Maximum initial contact angle (deg)</th>
<th>Minimum final contact angle (deg)</th>
<th>Hysteresis (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advancing/receding</td>
<td>124</td>
<td>100</td>
<td>24</td>
</tr>
<tr>
<td>Drop evaporation</td>
<td>119</td>
<td>110</td>
<td>10</td>
</tr>
</tbody>
</table>

From Table 5.2 the differences between the inherent hysteresis results obtained by the two methods significantly depended on the method used. In the advancing/receding method, the hysteresis was defined as the difference between the maximum advancing angle and the minimum receding angle. The reason for choosing this criterion was due to the fact that there were big
differences in the advancing angles. The moving contact line was very large in
the advancing/receding method. This lead to large variations in the advancing
angles caused by surface roughness. The same applies for the receding contact
angle. For the advancing/receding method, the measured contact angles were
considered dynamic contact angles, since the contact line was moving slowly.
The drop volume was increased from 5 microliter to approximately 20 microliter
at a rate of 10 microliter/min in the advancing stage. In the receding stage, the
volume was decreased from 20 microliter to approximately 7.5 microliter at the
same rate of 10 microliter/min. In the drop evaporation method, the hysteresis
was defined the same way (the difference between maximum initial contact angle
and minimum final contact angle). The reason for choosing this criterion was due
to the fact that the differences in the initial contact angles were very small
(differences between initial contact angles of independent trials).

In this study the initial static contact angles were the maxima, immediately
after dispensing the droplet on the coated surfaces. When contact angle was
measured immediately after dispensing the droplet, it gave the maximum contact
angle. After relaxation, the contact angle gradually reduces over time. The
reduction in contact angle passes through two stages. In the first stage, the
reduction in contact angle was small. However, in the second stage, the
reduction in contact angle was changing dramatically. The change in contact
angle occurs at relatively long time. Hence, the contact angles in this case were
considered static contact angles. The moving contact line was very small
compared to the advancing/receding method. As a result, fewer oscillations in contact angle were observed. The droplet decreased in size from 5 ± 0.15 microliter to 2 ± 0.27 microliters in 15 minutes.

The advancing/receding method was useful in characterizing the inherent hysteresis caused by the surface roughness. It gave insights on the large variations that can arise due to surface roughness. The drop evaporation method was useful in setting a reference time for applying voltage in electrowetting experiments.

Figure 5.6 and 5.7 showed that the drop in the first 400 seconds was relatively stable in both contact angle and drop diameters. For this reason, the timing for applying the voltage was chosen to be within 400 seconds from dispensing the droplets, in particular, between the fourth and fifth minute. This was the reference time for applying voltages to the drops in electro-hysteresis study, which is discussed in the following section.

5.4.3 Voltage short and long exposure time for electro-hysteresis study

The electro-hysteresis is defined as the difference between the average initial contact angle before applying the voltage and the average contact angle after applying the voltage and resetting the voltage back to zero. In general, the contact angle of the electrified drops does not return to the initial contact angle prior to applying the voltage. This is the electro-hysteresis caused by applying
the voltage. Electro-hysteresis study was carried out for both short and long exposure times. The study will be presented for four cases as will be demonstrated next.

For the short exposure time tests, 100 and 200 VDC were introduced to the drops in the two electrode orientations. The two electrode orientations were the vertical electrode and the horizontal electrode described earlier in Chapter III. In the short exposure time tests, the gap distance between the wire electrode and the flat electrode was 600 ± 50 $\mu m$. Short exposure time tests were performed as the following:

1) 100 VDC with the vertical electrode for 1.5 seconds (One pulse mode).
2) 100 VDC with the horizontal electrode for 1.5 seconds (One pulse mode).
3) 200 VDC with the vertical electrode for 2 seconds (One pulse mode).
4) 200 VDC with the horizontal electrode for 2 seconds (One pulse mode).

These cases are discussed in details in this section. The electro-hysteresis results will be summarized at the end of this section.

1) 100 VDC with the vertical electrode for 1.5 seconds (One pulse mode).
   The vertical wire electrode was used for this test. Voltage was introduced for approximately 1 second (short exposure time). The voltage was applied after roughly 1.5 seconds from recording the videos. The gap between electrodes was
600 ± 50 μm. The voltage was introduced to the drops between the fourth and the fifth minute from dispensing the drops. Figure 5.8 shows contact angle and drop base diameter change as a function of time.

Figure 5.8 shows the change in contact angle and drop base diameter as a function of time. The electro-hysteresis in this case was 4° The change in contact angle can be calculated from the slope of the line. Contact angle change occurred in a rate of 124 degrees/second. The figure also shows the contraction of the drop base diameter after applying the voltage. The drop base diameter did not go back to the original length as shown in the figure. The increase in base diameter was 93 μm.
2) 100 VDC with the horizontal electrode for 1.5 seconds (One pulse mode).

In this case the horizontal wire electrode was used. The gap between the electrodes was $600 \pm 50 \mu m$. 100 VDC was applied to the drops for a short period of time, for 1 second. The voltage was introduced to the drops after 1.5 seconds from recording the videos. The voltage was applied between the fourth and fifth minute from dispensing the liquid droplets on the coated surfaces. Figure 5.9 shows the change in contact angle and base diameters of the droplet for this case.

![Graph showing contact angle vs time and base diameter vs time](image)

Figure 5.9. Short exposure time tests in the horizontal electrode arrangement (one pulse mode). 100 VDC case, the voltage was applied for 1 second after roughly 1.5 second from recording the video of the electrified drops. The electro-hysteresis in this case is $6^\circ$. The increase in drop base diameter is $205 \mu m$. 
Figure 5.9 shows the change in contact angle and drop base diameter as a function of time. Electro-hysteresis in this case was calculated and found to be 6° (difference between the averaged initial and final angles). From the slope of contact angle curve the change was 90 degrees/second. The figure also shows the difference in the drop base diameter. The base diameter did not return to the initial base diameter. The increase in base diameter was 205 μm (difference between average initial base diameter and average final base diameter).

3) 200 VDC with the vertical electrode for 2 seconds (One pulse mode).

In this case the vertical electrode was used. The gap between the electrodes was 600 ± 50 μm. 200 VDC was introduced to the drops for 2 seconds after roughly 1.5 seconds from starting the video recording. The voltage was introduced to the drops between the fourth and fifth minute from dispensing the drops on the coating surfaces. Figure 5.10 shows the change in contact angle and the drop base diameter as a function of time.
Figure 5.10. Short exposure time tests in the vertical electrode arrangement (one pulse mode). The 200 VDC case, the voltage was applied for 2 second after roughly 1.5 second from recording the video of the electrified drops. The electro-hysteresis is 5°. The increase in drop base diameter is 122 \( \mu m \).

Figure 5.10 shows contact angle and drop base diameter as a function of time. Electro-hysteresis was calculated and found to be 5° (difference between the initial and final angles). The plot also shows that the change in contact angle passed through two stages. The first stage has a slope of 130 degrees/second and the second stage has a slope of 24 degrees/second. The second slope might be an indication of reaching contact angle saturation. The plot also shows the change in base diameter. The increase in base diameter was 122 \( \mu m \) (difference between average initial base diameter and the average final base diameter).
4) 200 VDC with the horizontal electrode for 2 seconds (One pulse mode).

The horizontal electrode was as used in this test. The gap between the electrodes was 600 ± 50 $\mu$m. 200 VDC was introduced to the drops after 1.5 seconds from recording the video. The voltage was introduced between the fourth and fifth minute from dispensing the drops. The short exposure time test was conducted for the horizontal electrode arrangement. However, the droplets were observed to move out of the imaged frame. Hence, no data could be obtained for this configuration. In this configuration, the droplets were not stable and movement of the droplets prevented performing electro-hysteresis study for this configuration. A detailed study on droplet movement will be given in Chapter VI.

For the long exposure time test, the voltage was applied in steps. Starting with 10 volts every 1.5 second until 200 VDC is reached, and setting the voltage back to zero at the end. This test was done for the same gap distance of 600 ± 50 $\mu$m and the two electrode configurations. Two case were studied as the following:

I. 200 VDC with the vertical electrode for 30 seconds (Stepwise mode).
II. 200 VDC with the horizontal electrode for 30 seconds (stepwise mode).
The goal of this test was to compare electro-hysteresis obtained from short exposure time test with the long exposure time test. The method of applying the voltage in this test was different. This allowed for conducting electro-hysteresis study for the 200 VDC with the horizontal electrode, which was not possible for short exposure time tests.

I. 200 VDC with the vertical electrode for 30 seconds (Stepwise mode).

The vertical electrode was used in this case. The gap between the electrodes was 600 ± 50 μm. The voltage was introduced to the drops between the fourth and fifth minute from dispensing the droplets on the coated surfaces. Figure 5.11 shows the change in contact angle as a function of time and applied voltage.
Figure 5.11 Contact angle change measured for the long exposure time test (stepwise mode). The vertical electrode orientation was used with 600 ± 50 μm gap distance. The voltage was applied in steps. The time interval for each step was 1.5 seconds. Electro-hysteresis in this case is 3°. The orange line represents the interval that has less contact angle reduction, which corresponds to the voltages above 100 VDC. The change in contact angle in the second stage was less than that in the first stage.

Figure 5.11 shows contact angle change as a function of time and the applied voltage. The voltage was applied in steps, 1.5 seconds for each step. The electro-hysteresis for this case was 3° (difference between averaged initial and final angles). It can be seen from the graph that the change in contact angle beyond 100 VDC was slightly different than the change in contact angle before 100 VDC. The change in contact angle was lesser than the proceeding stage indicating that a saturation stage is approaching.
For this configuration, the drop base diameter was plotted as a function of time. Figure 5.12 shows the change in drop base diameter as a function of time. The data represents the change in base diameter for the drops used in the vertical electrode test with 200 VDC (stepwise mode).

Figure 5.12. Drop base diameter for the vertical electrode arrangement with 200 VDC applied voltage (stepwise mode). This instrumental error is 3%. The error bars represents one standard deviation. The increase in the base diameter was 65 $\mu m$. This plot is for the drops represented in Figure 5.11.

Figure 5.12. shows that the change in drop base diameter took place in steps corresponding to the change in contact angle presented earlier in Figure 5.11. The increase in drop base diameter in this case was 65 $\mu m$ (the difference between the averaged initial and averaged final base diameter).
II. 200 VDC with the horizontal electrode for 30 seconds (stepwise mode).

The horizontal electrode was used in this case. The gap between the electrodes was 600 ± 50 μm. 200 VDC was applied to the drops between the fourth and fifth minute form dispensing the drops on the coated surfaces. The voltage was applied in steps. Each step was for 1.5 seconds. Figure 5.13 shows contact angle as a function of time and the applied voltage.

![Graph](image)

Figure 5.13. Contact angle change measured for the long exposure time test (stepwise mode). The horizontal electrode orientation was used with 600 ± 50 μm gap distance. The voltage was applied in steps. Each step was for 1.5 seconds. Electro-hysteresis in this case is 8°. Beyond 100 VDC, the change in contact angle was less than that prior 100 VDC. The change in contact angle in the second stage was less than that in the first stage indicating that saturation stage was approaching.

Figure 5.13 shows contact angle as a function of time and the applied voltage. The electro-hysteresis in this case was 8°(difference between the averaged initial and averaged final angles). The graph also shows a second stage of contact angle reduction. The change in contact angle in the second
stage was less than that in the first stage, indicating that the saturation stage was approaching. This second stage was for the contact angles beyond 100 VDC as shown in the graph by the orange line.

For this configuration, the drop base diameter was plotted as a function of time. The plotted data is for the drops presented in Figure 5.13. This case was for the 200 VDC with the horizontal electrode (stepwise mode). Figure 5.14 shows the change in drop base diameter as a function of time.

![Figure 5.14. Drop base diameter for the horizontal electrode arrangement with 200 VDC applied voltage (stepwise mode). This instrumental error is 3%. The error bars represent one standard deviation. The increase in the base diameter was 254 μm. The plot represents the change in base diameter for the drops presented in Figure 5.13.](image)
Figure 5.14 shows that the change in drop base diameter took place in steps corresponding to the change in contact angle presented earlier in Figure 5.13. The increase in drop base diameter in this case was 254 \( \mu m \) (the difference between the averaged initial and final base diameter). A summary of electro-hysteresis study is presented in Table 5.3. Also, a summary of the drop base diameter results is given in Table 5.4.

Table 5.3 Summary of contact angle electro-hysteresis for all cases.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Figure #</th>
<th>Initial angle (deg)</th>
<th>Final angle (deg)</th>
<th>Electro-hysteresis (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical 100 VDC</td>
<td>Figure 5.8</td>
<td>114</td>
<td>110</td>
<td>4</td>
</tr>
<tr>
<td>(One pulse mode)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Horizontal 100 VDC</td>
<td>Figure 5.9</td>
<td>112</td>
<td>106</td>
<td>6</td>
</tr>
<tr>
<td>(One pulse mode)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vertical 200 VDC</td>
<td>Figure 5.10</td>
<td>114</td>
<td>109</td>
<td>5</td>
</tr>
<tr>
<td>(One pulse mode)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vertical 200 VDC</td>
<td>Figure 5.11</td>
<td>114</td>
<td>111</td>
<td>3</td>
</tr>
<tr>
<td>(Stepwise mode)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Horizontal 200 VDC</td>
<td>Figure 5.13</td>
<td>113</td>
<td>105</td>
<td>8</td>
</tr>
<tr>
<td>(Stepwise mode)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
By examining the results in Table 5.3 electro-hysteresis was the highest in the horizontal electrode configurations, in general. Electro-hysteresis was 6° for the horizontal electrode in the 100 VDC (one pulse mode). Electro-hysteresis study could not be conducted for horizontal electrode with the 200 VDC (one pulse mode) as mentioned earlier. However, for the 200 VDC and horizontal electrode (stepwise mode) the electro-hysteresis study was conducted and was found to be 8°. The voltage was applied in steps in the stepwise mode, this allowed for completing the test without the problem of the droplet moving. Despite this fact, the droplet was not stable and that is shown by the high hysteresis result. The highest electro-hysteresis was found in the stepwise mode for the horizontal electrode arrangement. The lowest electro-hysteresis was for the stepwise mode for the vertical electrode, and was found to be 3°. In the 100 VDC (one pulse mode) the electro-hysteresis for the vertical electrode was found to be 4°. In the on pulse mode and vertical electrode, the electro-hysteresis was less than that for the horizontal electrode with the one pulse mode. This indicates that in the same voltage mode and voltage magnitude, the vertical electrode gives less electro-hysteresis, 6° with the horizontal electrode compared to 4° in the vertical electrode (one pulse mode). This observation was also found with in the 200 VDC (stepwise mode). In this case, electro-hysteresis was 8° in the horizontal electrode compared to 3° in the vertical electrode (stepwise mode).
Table 5.4 shows the increase in drop base diameters for all studied in electro-hysteresis cases. The increase in drop base diameter was based on the averaged initial and final drop base diameter. The increase in drop base diameter is another indication of electro-hysteresis effect. The drop base diameter did not go to the initial drop base diameter due to the applied voltage. As demonstrated in the literature review in Chapter II, this is the effect of charge trapping in the dielectric. The horizontal electrode in both voltage modes (one pulse mode and
stepwise mode) gave the highest increase in base diameter. The increase in base diameter was 205 \( \mu m \) for the 100 VDC (one pulse mode) for the horizontal electrode. Furthermore, the increase in drop base diameter for the horizontal electrode in the 200 VDC (stepwise mode) was 254 \( \mu m \). This increase was due to the fact that the droplet in this configuration was not stable. For the vertical electrode case, the increase in drop base diameter was 93 and 122 for the 100 VDC and 200 VDC cases (one pulse mode). For the stepwise mode and 200 VDC, the increase in drop base diameter was 65 \( \mu m \).

In general, these results showed that voltage magnitude and mode affects the electro-hysteresis. In addition, electro-hysteresis was higher in the horizontal electrode than in the vertical electrode regardless of the mode used. This indicates that the horizontal electrode affects the stability of the droplets with applied voltage.

In summary, contact angle hysteresis results and drop base diameter analysis gave insights about the differences in electrowetting performance. The electrode configuration has a big effect on contact angle electro-hysteresis.

5.4.4 Experimental and predicted contact angle for the two electrode orientations

The contact angle change with the applied voltage was studied for both electrode orientations in two electrode-electrode gaps. The vertical gap may have effects on the shape of the droplet and hence contact angle. The two gaps
used in this study were 600 and 1000 ± 50 μm. To compare the shape of the droplet in the 600 ± 50 μm gap, a drop was placed on a stainless steel coated surface. After that, images of the same drop were taken in three configurations as shown in Figure 5.15.

![Figure 5.15](image-url)

Figure 5.15 Images taken for the same drop with different electrode configurations. A) with no electrode. B) with the vertical electrode. C) with the horizontal electrode. The electrodes were placed on the droplet in the same order they appear in the image. The time it took to take images of the drop with different electrodes was approximately 1 minute. Two adjustable electrode holders were used. The shape of the droplet was not significantly affected by the electrode orientation. The vertical electrode penetrated the drop, while the horizontal electrode touched the drop from the outside. The voltage in these three cases was zero.

In the 600 ± 50 μm gap the shape of the droplet was not affected by the electrode orientation. In contrast, with the 1000 ± 50 μm gap the shape of the droplet was significantly affected with the horizontal electrode orientation. The horizontal electrode experienced a mechanical force on the drop as shown in Figure 5.16.
To study contact angle change due to applied voltages, a drop was subjected to electrical potentials from 0 to 200 VDC in the two electrode orientations and $600 \pm 50 \mu m$ gap as shown in Figure 5.17. In each electrode orientation and gap a new drop was dispensed on the surface. The programmed voltage was applied afterwards.
Figure 5.17 Contact angle for the two electrode orientations. Voltage was applied in 10 VDC steps. Each step was 5 seconds apart. The electrode-electrode gap was $600 \pm 50 \mu m$. The data were obtained from three experimental trials. Each trial with a new drop on the surface.

The plot in Figure 5.17 shows the experimental contact angle for both electrode orientations deviated from the contact angle predicted by the Young-Lippmann Equation (2.5) almost in the same manner. The shape of the droplet was not affected significantly in this gap distance; this might explain this agreement between the vertical and horizontal electrode contact angles. At about 125 VDC and greater, the contact angle became nearly constant indicating the system approached a charge saturation effect. Generally the contact angle decreased, up to about 125 VDC, as predicted by the Young-Lippmann relation. Due to the charge saturations the contact angle became relatively insensitive to the voltage and for voltages greater than about 175 VDC the data deviates significantly from the predicted values.
For the 1000 ± 50 $\mu m$ gap, the horizontal electrode affected the shape of the droplet as it was seen earlier. The experimental contact angle is compared to the predicted contact angle in Figure 5.18 for both electrode orientations in this gap distance.

![Figure 5.18 Contact angle for the two electrode orientations. Voltage was applied in 10 VDC steps. Each step was 5 seconds apart. The gap was 1000 ± 50 $\mu m$. The data were obtained from three experimental trials. Each trial with a new drop on the coated surface.]

The experimental data points in Figure 5.18 more closely followed the predicted values from the Young-Lippmann equation than the data in Figure 5.17 for the smaller gap distance. The vertical electrode data were followed the Young Lippmann relation better than the horizontal electrode, which may be due to the geometry effect on the drop in the horizontal electrode configuration shown.
in Figure 5.16. Similar to Figure 5.17, the system approached a charge saturation effect above 160 VDC and the contact angle became insensitive to voltage above about 160 VDC.

In summery, the contact angle of the electrified drops can be affected by the electrode orientation, the gap distance, and the applied voltage. The effect varies depending on the position of the electrode and the mechanical force that the electrode applies to the electrified drops. The copper wire was 128 $\mu m$ in diameter, which means that the presence of the electrode in any configuration contributes to the contact angle modulation due to its large size.

5.5 Electrocoalescence study in the horizontal electrode arrangement

The material used in this investigation was the same material described in previous section. The coating was conducted the same way with the same polymer composition described in section 5.4. The horizontal electrode arrangement was used in this investigation. In this study the drops were imaged from two angles. The first one was to obtain the top view of the electrified drops. The second angle was to obtain the side view of the imaged drops. The two angles were obtained for the same pair of drops in each experimental trial.
5.5.1 Objectives

The objectives of this work were to

- Predict coalescence based on geometrical considerations.
- Assess the speed of coalescence based on the voltage mode.
- Use high-speed imaging to examine the shape of the moving interface.

5.5.2 Imaging setup and voltage modes

There were two cameras used for this investigation. The first one was a CCD camera with 62 fps imaging capability used for the side view imaging. The second one was the high-speed camera with 500 fps imaging capability used for obtaining the top view images. A schematic of the imaging platform is shown in Figure 5.19.

![Figure 5.19 The two-camera system. The two light sources were used to provide back illumination for the imaged drops.](image-url)
In the experiments in this section the electrical potential was applied to the drops in two methods. In the first method voltage was applied directly by the programmable power supply described in Chapter III. In the second method the electrical potential was passed through a relay power switch, also described in Chapter III. The programmable power supply provided 200 VDC with slew rate demonstrated earlier in Chapter III. The relay power switch provided 200 VDC in a sudden step change. The relay was also used to introduce a voltage square wave for 0.1 seconds in an on/off mode.

5.5.3 Theoretical prediction of electrocoalescence

Coalescence of colliding drops can be hindered by many mechanisms as reviewed in Chapter II. Despite this fact, it was never been observed that two droplets in contact and did not coalesce in an electrowetting configurations. The coalescence in electrowetting configurations takes place on the coated surfaces. The movement of the droplet interfaces at the coated surfaces is the key factor in initiating coalescence. Once the droplet interfaces touch, the droplets rapidly coalesce due to electrowetting effect. The electrowetting effect drives the coalesced drop towards the minimum contact angle for that applied voltage. The limiting factor for non-coalescence in this study was bringing the droplets interfaces in physical contact. Hence, a model based on the geometry of two close drops was developed to predict coalescence. Based on the observed phenomena, it was assumed that once the droplet interfaces touch, coalescence takes place.
Figure 5.20 Schematic of two adjacent drops. A) showing the base radius and contact angle of the drops, and the separation distance between the drops. B) showing a hypothetical change in the same drops retaining their volumes but changing the base radius and contact angle.

Assuming that the drops can change their contact angles and hence the base diameter without any change in the drop volumes, the droplets interfaces approach each other due to the electrowetting phenomena. If the separation distance is small enough, the droplets interfaces can meet at a point where the droplet interfaces touch and coalescence occurs. Another assumption is that the center points of the droplets are fixed and the increase in the base diameter is symmetrical. Based on the geometry of the drops, equation 5.1 was derived. The derivation of this equation is in Appendix C. Equation (5.1) gives the radius of the circular contact line of the drop on the electrowetted surface as a function of the initial drop volume and the electrowetted contact angle. When the electrowetted drop radius satisfies the condition in equation (5.2) the drops will coalesce.

\[
a = \frac{3}{\pi} \frac{V_{\text{drop}}}{V_{\text{drop}}} \frac{\sin \theta (1 + \cos \theta)}{1 - \cos \theta + \sin^2 \theta}
\]

(5.1)
\[ a \geq (a_0 + 0.5b_0) \] for coalescence to occur \hspace{1cm} (5.2)

where

- \( a \): drop radius
- \( V_{drop} \): drop volume
- \( \theta_0, \theta \): initial and final contact angles
- \( b_0 \): initial separation distance
- \( b_c \): critical separation distance

In the range of conditions that the electrowetting experiments were conducted in this work, equation (5.2) can be solved for \( b_0 \) to estimate the distance between the drops when coalescence will occur due to electrowetting. The drop volume is fixed and the contact angle may change with the applied voltage. Theoretical distances can be calculated from the above expressions for different drop volumes as shown in Figure 5.21.
Figure 5.21. Theoretical critical separation distance (maximum separation distance) for electrocoalescence of adjacent drops in electrowetting configuration. The experimental critical distance was obtained for 5 microliter water droplets.

The theoretical curve in Figure 5.21 was calculated based on the initial contact angle which was 113° and the electrowetting contact angle which was 65°. The theoretical values were calculated by using equations (5.1) and (5.2). The experimental critical distance deviated from the theoretical value. This is due to the fact that the horizontal electrode was affecting the contact angle reduction as was seen in the previous section.

The experimental validation was conducted for one drop size, which was 5 microliter shown in the graph. Suggestions on extending this work will be given in The future work, in chapter IX.
5.5.4 Coalescence speed

As mentioned earlier, the speed of coalescence was rapid once the drops touched. Timed images of the coalescence of two drops are shown here. The voltage bias was 200 VDC. Top and side views of the electrified drops are shown in Figure 5.22 and 5.23. In this case the voltage was introduced in a slew rate mode. It takes 1.7 seconds to reach 200 VDC. However, the droplet reaches the maximum contact angle reduction at about 160 VDC as demonstrated earlier in Figure 5.18. After 160 VDC contact angle is not stable.
Figure 5.22. Side view of two drops, each drop is 5 microliter in volume. The voltage was introduced in a slew rate mode. It takes 1.7 seconds to ramp from 0 to 200 VDC. The drop-drop distance was 220 $\mu$m and the electrode-electrode gap was 1000 ± 50. The top electrode touched the droplets from the outside. The bottom electrode was dip coated ITO glass slide. The images were produced by the CCD camera, which skips frames due to its imaging limitations. These images were not used in any coalescence speed calculation.
Figure 5.23 Top view of the same pair of drops shown in Figure 5.22. It took about 608 milliseconds for the droplets to coalesce, from the moment of applying the ramping of the voltage. The coalescence of droplets occurred in 15 milliseconds from the moment the droplets interfaces touched.
The two cameras used for imaging operated at different frame rates. There are missing frames in the side view images. The side view images were produced by the CCD camera (62 fps). This means that not all top view images have side view images corresponding to them.

From the top view images produced by the high-speed camera, it took about 15 ± 5 milliseconds for the droplets to coalesce from the moment the droplets interfaces touched. The limiting step for coalescence to occur was establishing the physical contact between the droplets interfaces. The speed of coalescence depended on the rate at which the voltage was applied. It takes 1.7 second to reach to 200 VDC. From the top view images, coalescence took place at a shorter time. This means that coalescence occurred at a voltage less than 200 VDC. The separation distance between droplets was one factor for reducing the voltage necessary for coalescence. The separation distance between the droplets was 220 \( \mu m \). Coalescence took place at a contact angle less than the saturation contact angle at 200 VDC.
To compare coalescence speeds, 200 VDC was introduced by using the relay power switch for another pair of drops. The conditions were almost the same. The electrode-electrode gap was not difficult to control. The same Plexiglas holder was used with the same gap, insuring that the same electrode-electrode gap is used. However, the drop-drop distance was not easily controlled. Figure 5.24 and 5.25 show the top and side views of the coalescing drops, in the case where the relay was used.

Figure 5.24 Side view of coalescing drops. The relay power switch was used in this case. The coated electrode was ITO glass slides. The electrode-electrode distance was 1000 ± 50 μm. The voltage was 200 VDC applied in a sudden step change. Coalescence took place in a shorter time than what these images shows. The missing frames are shown for the top view in Figure 5.25. This was a limitation of the CCD camera.
Figure 5.25 Top view of the same pair of drops shown in Figure 5.24. Coalescence of the drops occurred in about 5 milliseconds from the moment the droplet interfaces touched. The whole coalescence event took place in about 16 milliseconds from the moment of applying the sudden step change of 200 VDC using the relay power switch.

From Figure 5.24 and 5.25, coalescence was very fast compared to the previous case. It took about $5 \pm 1$ milliseconds for the droplets to coalesce once the droplets established a liquid bridge between them. In addition the whole coalescence event took about 16 milliseconds compared to roughly 650 milliseconds in the slew rate mode. Clearly, the method of applying voltage has a
big effect on the speed of coalescence of two close drops. Also, by examining the shape of the droplets during coalescence, the movement of the droplets interfaces was significantly influenced by the method of applying the voltage. From the images, coalescence of the droplets was smoother in the voltage slew rate mode than in the sudden step change mode.

5.6 Electrocoalescence in the parallel electrode arrangement

In this set of experiments, electrocoalescence was conducted by using the parallel plate electrowetting configuration shown earlier in Chapter III. The flat electrodes were coated stainless steel plates. The separation distance between the plates was 1000 and 1500 ± 50 μm. Electrowetting effects take place at both sides inside the channel. Two voltages were used in this set of experiments with one powering mode. The mode was on/off square wave mode. The voltage was applied in periods by using the programmed relay power switch. The voltage was turned on for 0.1 second and turned off for 0.1 second, continuously. The rapid change in applying the voltage causes the droplets to vibrate. This vibration causes droplet interfaces to slightly shift with each cycle. Over time, the droplets may come in contact and coalesce due to this vibration. Figure 5.26 and 5.27 show two independent cases for coalescing drops via vibrating the droplet.
Figure 5.26 Coalescence of drops embedded between two coated stainless steel plates. The separation between the plates was around 1000 ± 50 μm. The voltage was 200 VDC applied in on/off mode for 0.1 seconds intervals.

From Figure 5.26, it took about 31.4 seconds for the droplets to coalesce. During this time the droplets vibrated due to the applied square wave voltage of 200 VDC. After coalescence, the droplet became 10 microliter in size. The time required for coalescence was long compared to the other cases. This is due to the fact that electrowetting takes place at both sides inside the channel. However, with the on/off mode the droplets can vibrate and chances of coalescence increases.
Figure 5.27 Coalescence of water droplets in the parallel electrode configuration. The electrode-electrode gap was roughly $1500 \pm 50 \mu m$. The applied voltage was 300 VDC with 0.1 seconds on/off mode.
From Figure 5.27, it took about 3 seconds for the droplets to coalesce. The droplet sizes were the same as the previous case. However, the voltage was increased to 300 VDC. The drop-drop distance and the electrode-electrode distance were different from the previous case. This might have effects on the speed of coalescence in the two cases. In any case, with the increase in voltage the droplets were observed to coalesce much faster than in the previous case.

5.7 Conclusion

In this chapter, experimental studies on electrowetting and electrocoalescence in air media were demonstrated. Electrowetting was studied for spin-coated films. It was also studied for dip-coated films. Contact angle hysteresis was studied for the droplets with and without the presence of the electrical fields. The effects of the wire electrodes on the electrified droplets were studied in different geometrical orientations. A model was developed for predicting electrocoalescence on coated surfaces. Electrocoalescence study was demonstrated for different electrode configurations.
6.1 Introduction

Manipulating small drops can be achieved by different means. One common approach is by taking the advantage of interfacial forces manipulation at the local domains. Surface tension force dominates for small drops. Hence, surface modifications can lead to small droplet motion. Chemically treated surfaces were used to control droplet movement (187, 190). One drawback of chemically treated surfaces is that the local surface energy is fixed and is dependent on functional groups attached permanently to the treated surfaces. Consequently, there are limitations on the droplet transport on these surfaces. Electrowetting is an attractive method for droplet transport applications.

6.1.1 Motivation

The ability to control droplet motion has many potential applications. As demonstrated earlier in the literate review, small droplet manipulation had applications in biomedical fields. In this project, tough, droplet movement control has advantages in the overall objective of the study.
6.1.2 Objectives

- Modify surface properties to control droplet motion.
- Experimentally, quantify the critical conditions for initiating droplet motion.

6.1.3 Hypothesis

- Gradient in dielectric layer induces electrical gradient on the coated conducting surface when subjected to electrical potential.
- Electrified droplets on gradient coating encounter unbalanced electrostatic force that leads to droplet motion towards the stronger local electrical field.

6.2 Experimental setup and materials

Droplet motion investigation was carried out in one electrode configuration. The horizontal wire electrode configuration was used for these investigations. The horizontal wire electrode was described in Chapter III. All coated surfaces were coated using the custom-made dip coater demonstrated in Chapter III. Different polymer concentrations were used in this investigation. Cases and discussions on droplet motion investigations will be given in the subsequent sections.
6.3 Droplet movement on slight gradient coatings

Two cases will be discussed in this section. The polymer composition in these two cases was poly (styrene-co-methyl methacrylate) /Toluene) (20%/80%) by mass. The dipping speed was 0.80 mm/s. The substrate was ITO glass slides. The voltage used was 200 VDC in a slew rate mode by the programmable power supply in the first case. In the second case, the relay power switch was used.

In this section, two different cases will be presented. The common key factor between these cases is the gradient in the coating. The results of coating characterization shown earlier in Chapter IV showed that there is a slight gradient in the coatings. It is concluded that this gradient in coating is the key factor in initiating droplet movement. The two cases are presented next.

6.3.1 Droplet movement on ITO glass slides dip-coated substrates (case 1)

The substrate used in this case was ITO glass slides dip-coated in 20% polymer composition solution. In this case the relay power switch was used to give a sudden step change of 200 VDC. The electrode-electrode gap was 1110 ± 20 μm. The dimensions of the glass slide were 2 by 3 cm. Figure 6.1 shows the important stages of the droplet movement on the coated ITO glass slide. From the figure, the droplet encountered a sudden change in its overall stability. There were big changes to the droplet shape after 2 milliseconds from applying the voltage. Large perturbations at the interfaces with the surrounding media can be seen in the images of the electrified drop.
Figure 6.1 Droplet movements on ITO dip-coated glass slide. The droplet volume was 5 microliter (case 1). The electrode-electrode gap was 1110 ± 20 μm. 200 VDC was applied in a sudden step change using the relay power switch. Detachment of the droplet was observed in this case. After the detachment stage, the droplet started moving in the direction of the thinner coating. The movement was slow. It took about 7 seconds for the droplet to stop moving. The high-speed camera was used in this case. The movement distance was 3050 ± 50 μm.

From Figure 6.1, the droplet showed a fast response to the sudden step change in voltage manifested in the changes of the droplet shape. 200 VDC was introduced in sudden step change by using the relay power switch, which was
programmed for 1 second exposure time. By inspecting the images of the droplet during the times 0 milliseconds to 34 milliseconds, it can be seen that the droplet was undergoing fast changes in the contact angle and overall stability. After 8 milliseconds from applying the voltage, the droplet totally detached from the top wire electrode. Furthermore, the droplet became charged by virtue of the introduced voltage. After that, the droplet went through a relaxation period. During the relaxation period the droplet moved $3050 \pm 50 \mu m$. It took the droplet to move this short distance about 7 seconds from the moment of applying the voltage. The movement of the droplet was towards the thinner coating side. The movement of the droplet occurred after the droplet detached from the top electrode and the voltage was 0 VDC at that time. The sudden step change in this case was applied for 1 second by using the programmed relay switch. The movement was during charge relaxation period.

6.3.2 Droplet movement on ITO glass slides dip-coated substrates (case 2)

The substrates used in this case were ITO dip-coated glass slides. The voltage used in this case was 200 VDC applied in slew rate mode. The polymer composition was 20%. The electrode-electrode gap was $225 \pm 20 \mu m$. The dimensions of the glass slides were 2 by 3 cm. The droplet moving distance was $3000 \pm 50 \mu m$. Figure 6.2 shows selected images of the moving drop.
Figure 6.2 Moving drop on ITO dip-coated glass slide. The voltage was 200 VDC applied in the slew rate mode. The electrode-electrode gap was 225 ± 20 \( \mu m \) s. The contact angle reductions occurred gradually accordingly with the rampage in voltage. The movement distance was 3000 ± 50 \( \mu m \) s.

Figure 6.2 shows the movement of 5 microliter water drop on coated ITO glass slide. The change in contact angle occurred during approximately the first second as shown in the image sequence in the 0 to 1020 millisecond frames. After that, the droplet started sliding towards the thinner coating side until it stopped moving. Finally, the voltage was set back to zero VDC. The moving distance was 3000 ± 50 \( \mu m \). A summary of the results obtained from the above two case is presented in Table 6.1.
Table 6.1 Summary of the results obtained in the two cases. In the two case, ITO glass slides were the substrates and 20% polymer solution was used for coating the substrates. The dipping was at a rate of 0.8 mm/s.

<table>
<thead>
<tr>
<th>Figure number</th>
<th>Power mode</th>
<th>Electrode gap (μm)</th>
<th>Moving distance (μm)</th>
<th>Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>Sudden step</td>
<td>1110 ± 20</td>
<td>3050 ± 50</td>
<td>7</td>
</tr>
<tr>
<td>Case 2</td>
<td>Slew rate</td>
<td>225 ± 20</td>
<td>3000 ± 50</td>
<td>3</td>
</tr>
</tbody>
</table>

From Table 6.1, the moving distances were very close for both cases. Regardless of the power mode used and the electrode-electrode gap, the droplets were moving in the same direction for both cases. For the first case, though, the time it took the droplet to move nearly the same distance, was large compared to the second case. The reason behind this was due to detachment of the droplet from the top electrode in the first case. Hence, the movement was driven by charge relaxation in the second case.

In all cases there were different mechanisms for droplet movement. The distance of movement was relatively short. It was interpreted that the droplet reaches the equilibrium symmetrical contact angle after moving then it comes to a halt. Also, It was interpreted that due to slight gradient in coating, the droplet reaches contact angle equilibrium shortly after the droplet movement.
6.4 Droplet movement on controlled gradient

The gradient on coating was controlled. The gradient in this case was characterized by using tabletop scanning electron microscopy (Model TM 3000 Tabletop microscope). The droplets were observed to move from the thicker coating region to the thinner coating region.

6.4.1 Dipping method

The polymer concentration was 35% poly (styrene-co- methyl methacrylate) and 65% Toluene by mass. The dipping procedure in this case was modified. The followed procedures produced a large gradient in the coating. The substrates were dipped with 0.3 mm/s dipping speed until the substrates were immersed in the solution. After that, the substrates were pulled out of the solution at 0.3 mm/s pulling speed. The following step was to use a holder to place the substrate in a horizontal position to let it air dry. The drying stage was for 24 hours in 22.5 ± .5 °C environment. Then, the substrate was dip coated in FluoroPel at 0.8 mm/s dipping speed. Figure 6.3 shows the cross section of the coating. The coating was carefully peeled off of the glass slides. After that, it was placed on an SEM stub for imaging. All slides were coated in the same coating procedures and produced similar coating profile.
Figure 6.3 SEM images showing the cross section of the coating (cross section along the vertical direction of the dipped substrate). The first frame shows the bottom part of the substrate, while the last frame shows the top part of the substrate. The gradient increases in the vertical direction. Thicker part is the part that is immersed first, and the thinner part is the part that is immersed last during dipping.

Figure 6.3 shows a sample of the gradient on the coated slides. Clearly, the thickness of the coating was decreasing towards the top portion of the coated glass slides. The physical properties of the solutions used for dipping had a big effect on the gradient formation. The viscosity of the 35% polymer concentration solution was the highest among the prepared solutions demonstrated earlier in Chapter IV. High viscosity contributed to the formation of the thicker part at the
bottom of the coated glass slide. Surface tension contributed to the formation of the thinner coating at the top of the glass slide. Both these two physical properties synergistically contributed to the formation of the gradient on the glass slides.

The consequence of applying voltage to the sessile drops on this gradient is that the drop encounters an asymmetrical change in contact angle. Contact angle change with the applied voltage was characterized. The droplets were placed approximately on the same spot in every test. The spot was about 1500 ± 500 \( \mu m \) from the edge of the thicker coating.

6.4.2 Contact angle characterization

Contact angle change due to the applied voltage was investigated. After many experimental trials, the voltage range for initiating the movement was identified. Figure 6.4 shows contact angle change of 5 microliter on the coated ITO glass slide. The droplet was placed at about 1500 ± 500 \( \mu m \) from the edge of the thicker side, in all contact angle characterization experiments and drop movement experiments, as well.
Figure 6.4. 300 VDC applied to 5 microliter water drops in the slew rate mode shown in the graph. The graph shows contact angle change as a function of time and voltage. Contact angle was calculated for the left and right angles of the drops and averaged for two experimental trials. The error bars represents on standared devation.

From Figure 6.4 Contact angle change was steady with the applied voltage. The droplet did not move in this set voltage. Hence, the voltage was increased to 400 VDC for the next trials, which is shown in Figure 6.5.
Figure 6.5. Contact angle change of 5 microliter water drops. The slew rate mode is shown in the graph. Contact angle curve represents the averaged value of contact angle at each moment in time. The averaged contact angle represents the left and right angles averaged for two experimental trial for new drops in each trial. The error bars represent one standard deviation.

Figure 6.5 shows the change in contact angle for the 400 VDC case. The same substrate was used. The droplet was placed on the same coated spot, as in the previous case. It can be seen from the plot that with the increase in voltage, there were more variations in the contact angle. This is an indication that the contact angle with this increased applied voltage was less stable than in the previous case. The droplet did not move at this voltage. Hence, the voltage was increased to 500 VDC for the next trials, which is shown in Figure 6.6.
Figure 6.6. Contact angle change of a 5 microliter water droplet on the coated substrate. 500 VDC was applied to the drops in the slew rate mode shown in the graph. There were big differences in the contact angle due to droplet instability with the increased voltage. The data represents two experimental trials. The error bars represent one standard deviation.

Figure 6.6 shows the change in contact angle for a 5 microliter water droplet placed on the coated ITO glass slide on nearly 1500 ± 500 μm from the thicker coating side. The plot shows that the change in contact angle was not stable at this increased voltage. The electrified droplet was encountering large perturbations in contact angle. The droplet in this voltage was hesitating to move, which explains the large variations in contact angles. The voltage was increased to 550 VDC for the next trials, which is shown in Figure 6.7.
Figure 6.7 Contact angle change of a 5 microliter droplet on the coated substrate. The slew rate used in this test is shown in the graph. The droplet moved out of the imaging frame at about 7.5 sec hence no data points appear after 7.5 sec. Contact angle reduction in this case was the maximum reduction in all case. The data were obtained for two independent trials. Each trail with a new drop. The error bars represent one standard deviation.

Figure 6.7 shows contact angle change of a 5 microliter drop. The droplet in this case moved out of the imaging frame and the software stopped performing contact angle calculation due to the absence of the drop from the imaging frame. Contact angle reduction in this case was the maximum among all cases. The voltage needed to reach the maximum angle reduction strongly depended on the coating thickness. Selected images of the moving drop are shown in Figure 6.8.
Figure 6.8 Moving droplet sitting on coated ITO glass slide. The Voltag used was 550 VDC. These images are for one of the experimental trials that was used for generating contact angle measurements represented in Figure 6.7.

Figure 6.8 shows selected frames of the moving drop. In this case, it took the droplet about 7.8 seconds to start moving. The voltage at this time reached approximately 510 VDC as shown in Figure 6.7. The asymmetric change in contact angle caused the droplet to move towards the thinner coating side. The
thinner side of the coating has less electrical insulation. Hence one side of the droplet responded to electrical field faster than the other side of the droplet. This caused an asymmetric change in contact angle. For the droplet to reach contact angle equilibrium, the droplet moves.

These images were produced using the CCD camera demonstrated earlier in Chapter III. The drops were magnified to meet the criteria required by the DSA, to allow it to conduct contact angle measurements automatically. More precise time characterization was conducted by using the high-speed camera.

In these coated surfaces, the contact angle change was stable for low voltages. As the voltage increased, the droplets became less stable, and that was clear from the demonstrated plots of the contact angle with the applied voltage. Furthermore, from contact angle measurements, the threshold voltage for initiating droplet movement was identified. The DSA has limitations in imaging; hence, the high-speed camera was used to investigate on the moving distance and required time for initiating the movement.
6.4.3 High-speed imaging for movement characterization

The high-speed camera was used to complete the investigation in the droplet movement experiments. The same coating method described in section (6.4.1) was used. Several videos were recorded of droplets moving on the coated substrates. Figure 6.9 shows image sequence of a moving drop on a coated substrate.
Figure 6.9. A 5 microliter drop moving on a coated substrate. The applied voltage in this case was 550 in the slew rate mode.
Figure 6.9 shows selected images of a moving drop in the coated substrate. This video was used to characterize velocity and distance of the moving drops. There were some limitations on the maximum distance that can be viewed with good resolution in both cameras. A summary of the analyzed videos is presented in Table 6.2.

Table 6.2  Droplet movement characterization on the controlled coating gradient. Data in this table were based on videos recorded by the CCD camera and the high speed camera.

<table>
<thead>
<tr>
<th>Actuation voltage (VDC)</th>
<th>Response time (sec)</th>
<th>Distance ((\mu m))</th>
<th>Velocity (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>530 ± 20</td>
<td>7 ± 1</td>
<td>17000 ± 1000</td>
<td>34 ± 1</td>
</tr>
</tbody>
</table>

Table 6.2 shows data that were calculated from the recorded videos. The actuation voltage is the voltage necessary for initiating the movement of the drops. This high voltage was strong enough to create a gradient in the electrical field in the insulating layer. Consequently, the drops feel unbalanced electrical forces acting on each side. As a result, an asymmetric change in the contact angle occurs and initiates the droplet movement. The actuation voltage in this investigation was found to be 530 ± 20 VDC applied in slew rate mode.
The response time is the time it took the droplet to change its contact angle. After that, the droplet moves a distance of 17000 ± 1000 μm. The average time and distance was calculated to give an average velocity of 34 ± 1 mm/s. The time used for calculating the velocity was the time of movement which was 0.5 ± 0.1 seconds.

In general, surface energies of the coatings had major effects on the electrified droplets stability. The surface energies of the coatings were obtained experimentally. They were found to be 36 ± 1.0 mN/m for the dielectric layer, whereas, it was found to be 13.5 ± 0.5 mN/m for the hydrophobic layer. It was expected to have low value for the surface energy of the hydrophobic layer. Teflon (PTFE) is a typical hydrophobic material with surface energy of 20.24 mN/m (191). Teflon is well known for its hydrophobicity due to its low surface energy.

The surface energies are expected to change by applying an external voltage as suggested by Lippmann relation (demonstrated earlier in Chapter II). Surface energy decreases with applying voltage, however, the decrease in surface energy can not be in negative values which is known to be the thermodynamic limit (as discussed in the literature section of this thesis).
6.5 Conclusion

In this chapter, droplet movement investigation was carried out. The droplets in all cases were 5 microliter in size. The movement of the droplets was investigated for slight gradient coatings. The distance of movement on the slight gradient was relatively short. Hence, a dipping method was developed to create large gradients. The movement of the droplets was significantly enhanced by the large gradient.
CHAPTER VII

ELECTROCOALESCEENCE IN DIESEL MEDIA

7.1 Introduction

Electrowetting and electrocoalescence phenomena were extensively studied in air media in the pervious chapters. In this chapter, electrocoalescence was investigated in diesel media. The investigations were conducted for relatively large drops and fine drops, as well. The continuous phase in these experiments was ultra low sulfur diesel. All electrocoalescence experiments demonstrated in this chapter were conducted for stationary fluids in a transparent diesel bath. The experimental setup and the results will be shown next.

7.2 Experimental setup

The horizontal electrode was used for all experiments in these investigations. The horizontal electrode arrangement was shown earlier in Chapter III. The voltages used in these investigations were in slew rate mode discussed earlier in chapter III. A transparent diesel bath was designed for conducting these experiments. The coated substrates and the electrode holder were immersed in diesel. Figure 7.1 shows an image of the experimental setup.
This setup was used for all electrocoalescence experiments. The figure shows the diesel bath placed on the DSA stage. The images of the coalesced drops were produced using the CCD camera that is attached to the DSA (demonstrated earlier in Chapter III).

Figure 7.1. An image of the diesel bath used in electrocoalescence experiments. The illuminated setup is used for obtaining side view images of the coalescing drops. The coated substrate is placed in the bath and the electrode holder is placed in the bath, too. The wire and coated substrate electrodes are connected to the power supply. The diesel bath is sitting on the DSA stage for imaging. Backfield illumination is used for obtaining side view images.

Figure 7.1 shows the electrowetting setup for producing images of the submerged drops in diesel. The illumination in this case, was set for obtaining side view images of the electrified drops. The light source faces the camera to obtain a bright field image, while the drops appear black in the images. The
diesel bath was also used for experiments when the high-speed camera was used. In the high-speed imaging platform, the diesel bath was illuminated from below and the high-speed camera was positioned above the diesel bath as shown in Figure 7.2. In this case, the transparent ITO glass slides were used as the coated substrates, though.

![Figure 7.2 Electrocoalescence imaging platform. This setup is used for obtaining top view images of coalescing drops submerged in diesel. The high-speed camera is used in this setup. The opening at the center allows for backfield illumination for the imaged drops. This setup is used with the transparent ITO glass slides.](image)

The automated syringe was used to dispense water droplets in the diesel bath. Due to viscous and buoyance forces, the positions of the droplets were not easily controlled. Some droplets will be in direct contact with both electrodes while other droplets may not be in direct contact with both electrodes. Also,
diesel may form a thin film on the coated substrate and the wire electrode. Nonetheless, electrowetting and electrocoalescence phenomena were observed to take place in these configurations.

7.3 Electrocoalescence of relatively large droplets

Deionized water droplets were used in this study. The droplets were dispensed using the automated syringe. Two cases were studied, the first one was with a coated stainless steel substrate and the second one was with a coated ITO glass slide (transparent slides). The two cases are presented next.

7.3.1 Electrocoalescence on dip coated stainless steel substrates

The substrates in this case were stainless steel plates cut into 1 by 3 cm. The substrates were dipped in 15% polymer concentration. After that, the coated substrates were dipped in FluoroPel; both dipping was at 0.8 mm/s speed. The cleaning procedures and dipping procedures were explained earlier in Chapter IV. 100 VDC was introduced to a pair of drops in slew rate mode. Electrocoalescence of the droplets was videotaped using the CCD camera. Figure 7.3 shows selected images from the video sequence.
Figure 7.3. Side view images of two water droplets submerged in diesel. The coated substrate was dip coated stainless steel substrate. The backfield illumination used in this setup made diesel phase appears transparent in these images. The droplets were 5 microliter in size. 100 VDC was applied in slew rate mode. The droplet to the right was touching the wire while the droplet to the left was not touching the wire. The CCD camera was used in this case.

Figure 7.3 shows selected frames from the image sequence of two coalescing drops. The drops were sitting on a dip coated stainless steel plate. In the second frame at time 600 milliseconds, the drop to the right was touching the
top wire electrode. The drop that was touching the wire electrode responded to the applied potential and reduced its contact angle. This is also shown in the following frame with time stamp 720 milliseconds with more reduction in contact angle. Contact angle reduction caused the surrounding diesel phase to move. The movement of the two phases (water and diesel) caused the second droplet (to the left) to move towards the electrowetted droplet (to the right). The next frame shows the coalesced drop at a time stamp 780 milliseconds. The blur in the coalesced drop was caused by the relatively low speed imaging capability of the CCD camera. The voltage at this time was on. The coalesced droplet was touching the top wire electrode, hence, the contact angle reduction continued with the applied voltage being on. After that, the voltage was set back to zero VDC and the coalesced droplet returned to the hydrophobic contact angle in the last frame with time stamp 2880 milliseconds.

The same setup, same voltage potential of 100 VDC, and same coated substrate were used for coalescing four drops. Figure 7.4 shows the coalesced drops images. The sizes of the drops ranged from 3 to 5 microliters. Some drops were touching the top wire electrode and some drops were not touching both electrodes.
Figure 7.4. Side view images of four water droplets submerged in diesel. The sizes ranged from three to five microliter. The continuous phase was diesel. The illumination used in this setup made diesel appears transparent in these images. The applied voltage was 100 VDC in applied in slew rate mode. The four drops coalesced into one drop. The CCD camera was used in this case. The substrate was dip coated stainless steel plates. Other drops in the distant background can be seen inside of the white interior of the larger drops, but did not have an effect on the electrowetting and coalescence of the drops in the foreground.
From Figure 7.4, three drops coalesced to form one bigger drop shown in the time stamp 300 millisecond. The voltage was 100 VDC applied in slew rate mode. The voltage was on until coalescence of the two droplets was achieved at 1100 millisecond. After that the coalesced droplet was reducing its contact angle with the presence of the electrical field (not shown in the selected images). Finally, the voltage was turned off and the droplet showed a nearly spherical shape in the last frame with time stamp 3800 milliseconds.

The two cases presented in this section, showed that coalescence of water droplets submerged in diesel took place by virtue of electrowetting phenomena via contact angle reduction. Due to buoyancy forces and surface properties, the droplets were nearly spherical in diesel fuel. With the presence of the applied potential, the change in contact angle and the overall electrostatic stability drove coalescence of the droplets. Coalescence of the droplets occurred on the electrowettable surface by virtue of electrowetting phenomena.

In the cases shown in Figure 7.3 and 7.4, the CCD camera was used for imaging. There were missing frames due to the imaging capability of the CCD camera. Also, top view images with lighting from above were not adequate to show the position of the droplet relative to the wire electrode. For these reasons, the high-speed camera was used to produce top view images on transparent ITO glass slides with background lighting from below.
7.3.2 Electrocoalescence on dip coated ITO glass substrates

The substrates in this case were ITO glass slides. The polymer concentration used to coat the glass slides was (10%/10%/80) (poly (styrene-co-methyl methacrylate)/Krytox/Toluene) by mass. The high-speed camera was used to capture coalescence events. The ITO glass slides were optically transparent. This advantage allowed for obtaining top view images of the coalesced drops using background lighting from below the slide. Figure 7.5 shows selected images of coalescence events. The applied voltage was 200 VDC in slew rate mode.
Figure 7.5. Top view images of four drops submerged in diesel. The substrate is ITO dip coated glass slide. The glass slide is transparent. The transparent substrate and the electrode holder were submerged in the diesel bath. The wire electrode is the top solid line indicated by the arrows in the images. Other lines and features are reflections from Plexiglas holder and the diesel bath. The applied voltage is 200 VDC in slew rate mode. High-speed camera is used in this case.
Figure 7.5 shows top-view images of coalescing drops. The substrate was transparent ITO dip coated glass slides. The continuous phase was diesel. The Plexiglas diesel bath and the Plexiglas electrode holder had scratches on them that appear in the images. Those features appear in the images sequence due to light reflection by the scratches. The top wire electrode is the horizontal line indicated by the arrow in the images. The second horizontal line was a reflection from the Plexiglas holder and was not a physical object in the presence of the diesel fuel or the drops. The applied voltage in this case was 200 VDC in slew rate mode. In the figure, after 230 milliseconds from applying the voltage, a liquid bridge formed between two close drops. After that, the two liquid droplets coalesced to form one droplet, shown in the 246-millisecond time stamped image. The voltage was still on and due to movement of the coalesced drop the second liquid bridge formed between the two drops shown in the 524-millisecond time stamped image. After the liquid bridge formation, the two drops coalesced to form one drop shown in the 532-time stamped image. The droplet increased in size and was not stable. The droplet moved due to electrostatic attraction towards the droplet that is touching the top wire and formed a liquid bridge. After the bridge formation shown in the 900-millisecond time stamped image, coalescence took place as shown in the 1048 time stamped image. The whole coalescence events took place in nearly 1 second.
High-speed imaging allowed for examining coalescence mechanisms. Two droplets come in contact form a meniscus between them. As demonstrated in the literature review in Chapter II, formation of meniscus does not necessarily leads to coalescence. In electrowetting configurations, though, it was observed that after meniscus formation coalescence take place in all cases. This is due to the fact that the droplets in electrowetting configurations may be charged by the introduced electrical potential. Hence, coalescence of droplets leads to a more stable state after coalesces. In addition, the coalesced drops respond to the applied voltage by reducing contact angle. Once the voltage is turned off, the droplet goes back to the hydrophobic state.

7.4 Electrocoalescence of fine droplets dispersed in diesel

Electrocoalescence of fine droplets was also achieved in the horizontal electrode arrangement. A solution was prepared by mixing 1 ml of deionized water with 100 ml of diesel to generate the dispersion in a beaker. After that the dispersion was transferred into the transparent diesel bath. The Plexiglas holder was adjusted to allow 100 ± 50 μm separation between the horizontal electrode and the coated ITO glass slide. 200 VDC was applied between the electrodes. Figure 7.6 shows selected images from the videotaped phenomena.
Figure 7.6 Top view images of fine droplets emulsified in diesel. The applied voltage was 200 VDC in slew rate mode. The voltage was applied for about 27 seconds. The separation between the wire electrode and the coated electrode was 100 ± 50 μm. The droplets were observed to migrate towards the horizontal wire. Coalescence of water droplets was observed near the horizontal wire.

Figure 7.6 shows top view images of dispersed water drops in diesel. The applied voltage was 200 VDC for 27 seconds. In about 1.5 seconds, small droplets coalesced to form bigger droplets as shown in the 1.583 seconds time stamped frame. The voltage was still on, and more droplets coalesced as shown in the 8.862 time stamped frame. The droplets were observed to move towards the energized horizontal electrode. Electrocoalescence mainly occurred near the
horizontal electrode. The last frame shows fewer dispersed droplet present than in the first frame due to coalescence of droplets. Droplets coalesced by two mechanisms. The first one was by direct contact with both electrodes via electrowetting. The second mechanism was driven by the electrical field gradient. The droplets migrated towards the strongest electrical field in their vicinity, which was the vicinity of the horizontal electrode. Since the gap distance between the horizontal electrode and the flat electrode was small (100 ± 50 μm s), the electrical field between the two electrodes was the strongest.

The frames shown in Figure 7.6 were recorded by using the high-speed camera at a frame rate of 1000 frames per second. It may be hard to distinguish the change in the fine drops positions in the selected frames. However, it was not practical to include large number of frames in this chapter. In fact, electrowetting and electrocoalescence were observed to take place between fine drops attracted by the energized electrodes. The droplets were driven by the electrical field gradient between the electrodes. Droplets were observed to wet the coated electrode without direct contact with the wire electrodes. The images were too dark due to high magnification and illumination difficulties and are not shown in this chapter.

Electrocoalescence of water droplets in diesel media showed that for relatively large drops, the dewetting time was less than a second. However, for finely dispersed water droplets the time for dewetting varied from 1 second to 10
seconds depending on the duration of applying the field. For example, if the field was applied for 1 second the dewetting occurs in 1 second. It was found that the dewetting depended on the duration of applying the field as well as the water concentration. That was a result of the fact that water concentration alters the dielectric property of diesel.

7.5 Conclusion

In this chapter, cases for coalescing discreet water drops were studied. It was observed that when the droplets were relatively large, electrowetting drives electrocoalescence of the droplets. The droplets first respond to the applied potential by reducing contact angle. Due to reduction on the contact angle, the droplet interfaces induce perturbation in the surrounding diesel medium. These perturbations cause movements of the droplets towards each other. Coalescence takes place between charged droplets near the energized electrodes after meniscus formation between the droplets.

Coalescence of finely dispersed droplets was also discussed. Fine droplets move towards the energized electrodes due to electrical field gradient in diesel. Coalescence of fine droplets takes place near the horizontal electrode due to electrostatic attraction. Coalescence of flowing dispersions will be discussed in the following chapter.
CHAPTER VIII

COALESCER DEVICE TESTING

8.1 Introduction

In the preceding chapter, electrocoalescence was studied in diesel media. Coalescence of fine drops was observed to take place between the energized electrodes. The fluids in those cases were stationary in diesel bath. In this chapter, coalescence of fine droplets in flowing dispersions through thin channel will be evaluated.

8.1.1 Hypothesis

- Coalescence of dispersed water droplets in diesel may be initiated by applying voltage to electrowettable surfaces.
- Dispersed water droplets are affected by the electrical field and can coalesce due to electrowetting effects, on the coated surface.
8.1.2 Objectives

- To build a compact coalescer device for testing the hypothesis.
- To evaluate the coalescer performance for coalescing fine drops in flowing dispersions.

8.2 Coalescer design and experimental setup

The coalescer was designed based on the learned facts from the conducted electrowetting experiments. The coalescer was designed based on the working range of the observed electrowetting and electrocoalescence experiments. To test the performance of the coalescer, the dispersions were prepared using a special experimental setup. The coalescer design and the experimental setup will be shown next.

8.2.1 Coalescer design

The coalescer consists of a stainless steel rod and a stainless steel tube. The rod was designed to be 19.00 mm in diameter and 11.00 cm long. The tube was designed to be 19.200 mm inside diameter. This design allows for 200 $\mu$m clearance between the rod and the tube when the rod is inserted inside the tube. However, the gap between the rod and the tube was measured by using a micrometer and found to be 190 ± 10 $\mu$m after machining the parts. This is may be due to human error in measuring the dimensions of the coalescer parts. It also may be due to slight differences in machining different parts of the coalescer. A
A schematic diagram of the coalescer is shown in Figure 8.1. Also, a schematic diagram of the top view of the cross section of the coalescer device is shown in Figure 8.2.

![Diagram of the coalescer device]

Figure 8.1. A schematic diagram of the coalescer device. The coated rod is inserted inside the tube to allow for 200 μm s gap between them. The dispersion flows through the gap between the rod and the tube.
Figure 8.2. Top view of the cross section of the coalescer device. The coated rod is inserted inside the tube. The coated rod is connected to the positive terminal of the power supply by a screw (not shown). Also, the tube is connected to the negative terminal of the power supply via another conducting screw (not shown).

Figure 8.1 and 8.2 show schematic diagrams of the coalescer device and the cross section of the device. Dispersion flows in the 200-μm gap between the rod and the tube. The rod is coated with the dielectric polymer followed by the hydrophobic polymer. The cleaning and dipping procedures were demonstrated earlier in Chapter IV. The polymer concentration used in coating the rod was 15%. The dipping speed was 0.8 mm/s.

8.2.2 Experimental setup

The coalescer device was connected to the dispersion setup. The dispersion setup consisted of dispersion tank for mixing ultra low sulfur diesel with water. The mixture is recycled into the tank by a centrifugal pump. The dispersion tank is also connected to a regulator valve for controlling the flow rate. A schematic diagram of the experimental setup is shown in Figure 8.3.
Figure 8.3 shows a schematic diagram of a generic setup. The coalescer parts are connected to the power supply via electrically conducting screws. It is also connected to the dispersion setup via proper tubing. Sometimes the coalescer outlet is connected to Jorin ViPA online particle sizing system (shown earlier in Chapter III). An image of the setup with the Jorin ViPA used in this case is shown in Figure 8.4. A close up image of the coalescer device is shown in Figure 8.5.
Figure 8.4. Dispersion setup. The Jorin ViPA is used in this case. Also, samples from the effluent dispersion can be characterized by using the Accusizer (demonstrated in Chapter III). Jorin relies on high speed imaging for generating particle size distribution.

Figure 8.5. Close-up of the coalescer device. The coalescer device is connected to the power supply via the red and yellow wires.
Figure 8.4 and 8.5 show the experimental setup for characterizing the performance of the coalescer. The power supply is connected to the relay power switch to provide the coalescer with the set voltage needed (as demonstrated earlier in Chapter III).

8.2.3 Dispersion preparation

3 milliliters of deionized water was added to approximately 11 liters of diesel in the dispersion tank. The mixture was stirred in the tank for 20 minutes using a stirrer. After that, the stirrer was removed. During the stirring, the centrifugal pump was recycling the dispersion for enhancing mixing. The recycle pump was operating throughout the testing time of the coalescer device, which is usually 30 minutes.

The stability of the dispersion in the flowing field was demonstrated and studied by Grace (192). The correlations give a relationship between the capillary effects and viscosities of the dispersed and continuous phases effects on the stability of the dispersions (193, 194). The dispersed drops may break up due to elongations induced by shearing flow. Depending on the capillary number and the relative viscosity, the region of drop break up due to shear flow can be identified.
For the prepared dispersion, the mean value for water drops was about 1 micron. The capillary number for the studied system was 10 and the relative viscosity was 0.061. Under these conditions, as suggested by Grace curves, drops do not break up in this flow field. This agrees with the experimental results of the samples taken from sample point 2. The drop size distribution of the inlet and outlet was compared. The distributions were almost identical, indicating that the dispersed drops were not affected by the shear flow. However, the coalesced drops after applying the electrical field may be affected by the flow field. This will be discussed in the discussion section.

8.3 Results and discussion

The coalescer was tested for coalescing drops. The flow rate of the dispersion was 40 ml/min. The voltage was 200 VDC applied in an on/off mode. The voltage was applied for periods of 5 seconds, and then switched off for 5 seconds. The relay power switch was programmed to perform these cycles for 30 minutes. The effluent dispersion was characterized by two methods. The first method was by using the Accusizer particle counter (shown earlier in Chapter III). The second characterization method was by using the Jorin ViPA system (shown earlier in Chapter III). The first method allowed for quantitative analysis via obtaining drop size distributions. While the second method allowed for qualitative analysis via images of the flowing dispersions.
8.3.1 Drop size distribution by the Accusizer

The coalescer was challenged with the prepared dispersion. 200 VDC was applied to the coalescer for intervals of five seconds in an on/off mode by the relay power switch. The coalescer was running for 30 minutes in the 200 VDC on/off mode. After 15 minutes from starting the test, 100 ml sample of the dispersion was collected from the inlet to the coalescer (sample point 1) and sent to the Accusizer for drop size distribution analysis. While the Accusizer performing the analysis on the sample taken from the inlet, a 100 ml sample from the outlet (sample point 2) was collected for drop size analysis. Figure 8.6 shows the drop size distribution of the inlet and outlet samples taken roughly 15 minutes after the starting of the test.

![Figure 8.6 drop size distribution of the samples taken from the inlet and outlet after 15 minutes from applying the voltage. The voltage was applied in an on/off mode. The periods for the on/off modes were 5 seconds each. The Accusizer generated these distributions.](image-url)
Figure 8.6 shows drop size distribution of the inlet and outlet of the coalescer after 15 minutes from starting the test. The voltage was applied in 200 VDC in an on/off mode, 5 seconds each. The graph shows an average of roughly $1.5 \mu m$ drop size for the inlet. For the outlet distribution, it shows two modes, one at about $2 \mu m$ and the other one at about $5 \mu m$. The drop size has increased due to the applied voltage. The applied voltage caused the droplets to coalesce inside of the thin channel (the $200 \mu m$ gap).

The second comparison of the drop sizes was made for samples after 30 minutes from starting the test. Two samples were characterized the same way explained above. Figure 8.7 shows the drop size distribution of the sample collected after 30 minutes from starting the test.

![Figure 8.7 Drop size distribution of the inlet and outlet of the dispersion. The applied voltage was 200 VDC in an on/off mode. These samples were taken after 30 minutes from starting the test.](image-url)
Figure 8.7 shows the inlet and outlet drop size distribution of the samples taken 30 minutes after starting operating the coalescer. By examining the two graphs, one can see that the inlet drop size distributions were similar. The number of drops has decreased but the size distribution remained almost the same for the inlet samples. The decrease in the number of the drops of the inlet stream was attributed to coalescence in the dispersion tank. Coalescence of drops may occur in the dispersion tank due to Brownian motion and other mechanisms (discussed in the literature review in Chapter II). Because the inlet distribution was not constant overtime, samples of the inlet was collected and compared with samples from the outlet for each comparison.

The area under the curves for the outlet samples was different. This is an indication that the water mass in the two cases was different. The water content existing the coalescer was fluctuating. Water was accumulating inside the coalescer with different rates. This may be due to the changes in the inlet water concentration as suggested by the inlet water drop size distribution. The inlet drop size distribution has to be maintained, as will be suggested in the future work section.
To analyze the drop size distributions presented in Figure 8.6 and 8.6, mass balance on water was performed. The drops were fairly spherical in this size range. Hence based on the number of drops and density of water, mass balance was performed. Mass of water in the inlet stream and the outlet stream can be calculated by the following expression

$$\sum_{i}^{N} \rho_w \left( \frac{\pi}{6} d_i^3 \right) n_i$$  

(8.1)

where

$$\rho_w: \text{water density} \quad d_i: \text{drops diameter}$$

The following table summarizes the calculated mass of the inlet and outlet for the samples taken after 15 and 30 minutes after applying the voltage in the on/off mode. The calculated masses were based on the distributions shown earlier.

Table 8.1 mass of water calculated from the inlet and outlet drop size distribution

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water mass in (g)</th>
<th>Water mass out (g)</th>
<th>in - out (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>After 15 minutes</td>
<td>$3.5 \times 10^{-11}$</td>
<td>$4.5 \times 10^{-11}$</td>
<td>$-9.6 \times 10^{-12}$</td>
</tr>
<tr>
<td>After 30 minutes</td>
<td>$2.0 \times 10^{-12}$</td>
<td>$8.6 \times 10^{-11}$</td>
<td>$-8.3 \times 10^{-11}$</td>
</tr>
</tbody>
</table>
From Table 8.1, the calculated masses were based on the samples taken after 15 and 30 minutes from starting the experiment. The droplet size distributions showed that there was an increase in the drop sizes. However, the increase in drop size does not necessarily reflect the instantaneous change in the inlet stream drop size distribution. The inlet and outlet samples were collected nearly 2 minutes apart (time needed for collecting the outlet sample after collecting the inlet sample). However, it was observed that the drop size distribution was greatly affected by introducing voltage, had the coalescer given enough time.

To test the effects of the voltage on the flowing dispersions, the voltage was applied continuously in a separate experiment. Figure 8.8 shows the drop size distribution of the outlet drop size with the voltage being off and outlet drop size when the voltage was continuously applied.
Figure 8.8 Drop size distribution of the outlet samples. The sampling was done with no voltage being applied. Also, another sample was collected when the voltage was continuously applied. The curve representing the drop size distribution of the outlet stream is not visible in the graph. The drop count was very low due to the drop hold up inside the coalescer with the presence of the applied voltage (and may be coalescence inside the coalescer).

Figure 8.8 shows the drop size distribution for two samples. Both the samples were for the outlet stream, one sample with the field being off and the other sample with the field being turned on during the sampling. The graph shows that there is big difference between the two distributions (the distribution with the applied voltage is not visible in the plot). This indicates that when the voltage is turned on the drops were trapped inside the coalescer by virtue of the applied electrical field. This performance was also observed in other experiments when the inlet drop size distribution was larger than the ones shown here. Images from Jorin ViPA confirmed the validity of this observation via images of the flowing dispersion, which will be show in the following section.
8.3.2 Drops images by Jorin ViPA system

The Jorin ViPA system implements relatively high-speed imaging technique for drop size distribution analysis (as demonstrated in Chapter III). The dispersion flows through a small window inside of the Jorin assembly, where flowing dispersion images can be captured by Jorin ViPA system. The dispersion was monitored by the Jorin ViPA system during the 5 second on/off mode. Figure 8.9 shows images of the flowing dispersion during the intervals where the electric field was in the on mode (during the 5 seconds applied voltage).
Figure 8.9 images produced by Jorin ViPA. These images are for the flowing dispersion when the voltage was in the 5 second interval and the 200 VDC was applied. Qualitatively, the number of drops in these images was very small compared to those when the voltage was not applied (will be shown in the next figure).

Figure 8.9 shows selected frames produced by Jorin ViPA system. The frames show almost absence of the dispersed droplets in diesel, when the voltage was in the on period (the five seconds). Unlike the case, when the voltage was off, in the five second period. Figure 8.10 shows images of the dispersed droplets as well as the coalesced droplets in the flowing dispersion in the off mode (the 5 second interval where the voltage was in the off mode).
Figure 8.10 images of the flowing dispersion at the five-second period when the field was in the 5 second off interval. The images show both the dispersed drops and the coalesced drop. After running the 5 second on/off mode for 15 minutes, the droplets inside the coalescer were released at the 5 interval off mode.

Figure 8.10 shows images of the flowing dispersion. These images were produced by the Jorin ViPA system. The images show the dispersed drops passing through the coalescer as well as the coalesced drops exiting the coalescer when the voltage was in the 5 second off period. The frames show drops that were in focus and some drops were out of focus.
Droplet size distributions indicated that voltage has great effects on the dispersed droplets. When the voltage was turned on continuously, there was a droplets hold up inside the coalescer. This was investigated via drop size distribution shown in Figure 8.8. It was also confirmed via the images shown in Figure 8.9. That was the reasoning behind choosing the 5 seconds on/off timing for applying the voltage, and characterizing the coalescer performance. The droplet size distributions shown in Figure 8.6 and 8.7 showed that there was a shift in the drop size distributions. However, from the mass balance shown in Table 8.1, the results showed increase in water mass that is exiting the coalescer. The mechanism in which these results can be explained is as follows:

1. Dispersion inters the coalescer.

2. Electrical field causes fine droplets to be electrically attracted to the electrified coalescer inside walls.

3. Coalescer accumulates coalesced water droplets inside the channel.

4. At a critical point, coalesced droplets flushes out of the coalescer by the flowing dispersion

This mechanism is postulated based on the droplet size distributions generated by using the Accusizer, and the images of the flowing dispersions generated by Jorin ViPA system. Electrowetting and electrocoalescence phenomena on coated surfaces showed that fine droplets can migrate and coalesce on the coated surfaces (as discussed in Chapter VIII). However, that
does not mean that coalescence of droplets was definitely stimulated by electrowetting effects. The presence of electrical fields in a thin channel can trigger other phenomena, such as dielectrophoresis. Dielectrophoresis can also induce coalescence of dispersed droplets (195, 196). In any case, electrical fields were believed to have positive effects on droplet coalescence in the presented design.

8.4 Conclusion

A coalescer device was introduced in this chapter. The design was based on the learned lessons from the results obtained in the previous chapters. The coalescer showed a proof of concept results, to a certain extent. The drop size increase was limited to 20 microns as was seen in the outlet distributions. This may be due to the fact that the flow field was affecting the coalesced drops stability. The critical capillary number suggested by Grace curves limited the increase in the drop size, in which the drops became vulnerable to breaking up by the flow field.

The coalescer device design needs to be reviewed and improved for practical applications. Suggestions on improving the performance of the device are given in the future work chapter, which is shown next.
CHAPTER IX

CONCLUSIONS AND FUTURE WORK

9.1 Introduction

Electrowetting and electrocoalescence phenomena were extensively studied in air and diesel media. Different electrode orientations and coating thicknesses were examined. Contact angle and the shape of the electrified drops were observed by using the high-speed camera. Electrified droplets showed interesting performance on the coated surfaces. In this chapter, conclusions on the achieved work will be demonstrated and suggestions for future work will be given.
9.2 Concluding remarks

The main objective of this work was to investigate on electrowetting phenomena to incorporate the phenomena in coalescing water droplets. The hypotheses were

- Coalescence of discrete water droplets on coated surfaces can be achieved by contact angle controllability via electrowetting phenomena.
- Coalescence of fine droplets can be achieved by virtue of electrical fields in electrowetting configurations.
- Small droplet transport can be achieved by electrical field gradient caused by coating gradient in electrowetting configuration.

Coalescence of discrete water droplet was achieved in air media as was shown in Chapter V. Contact angle modulation on coated surfaces was studied and critical conditions for achieving coalescence of water droplets in air media were demonstrated in Chapter V. In addition, coalescence of discreet water droplets was studied in diesel media. Chapter VII demonstrated the applicability of electrowetting phenomena on coalescing water droplets in close vicinity, in diesel media.
The presence of electrical field in electrowetting configuration proved to have effects on droplet stability as was shown in Chapter VI. The droplets were transported via electrical field gradient caused by coating gradient on coated surface.

Coalescence of fine droplets was achieved in diesel media in electrowetting configuration, in the presented coalescer prototype presented in Chapter VIII. This was detected by droplet size distributions and high speed imaging for flowing dispersions.

In general, overall objectives were achieved. However, the coalescer design needs further modifications for better coalescing performance. The limitation on the electrowetted coalescers lies in the condition of maintaining a small distance between the two electrodes. Suggestions on extending the achieved results are given in the following sections.

9.3 Effects of coating morphology

The dielectric coatings showed great effects on contact angle modulation in electrowetting phenomena. That was demonstrated in Chapters V through VII. There was one class of coating that was not tested for its effects on electrowetting phenomena, namely, the patterned coatings shown in Chapter IV. Suggestions on extending the work on patterned coatings are:
Testing the effects of the patterned coatings on contact angle, with and without the presence of the electrical fields.

Testing the effects of the patterned coatings on electrocoalescence of water drops along the grooves of the patterned coatings with the horizontal electrode arrangement.

Formulating a predictive model based on the physical properties of the solution and substrate for predicting the amplitude and wavelength of the patterned coatings.

9.4 Electrocoalescence in the horizontal electrode arrangement

Electrocoalescence in the horizontal electrode arrangement was driven by contact angle reduction on the coated surfaces. An expression was derived to predict coalescence of droplets in close vicinity (Chapter V). The expression was derived based on geometrical considerations. The expression has contact angle term in it. The suggestions are as the following

- Test other droplets sizes and compare with the prediction by the expression.
- Tests other coating system and compare results with the prediction by the expression.
- Incorporate interfacial tension in the expression via contact angle term.
9.5 Coalescer device modification

The coalescer device in Chapter VIII showed that coalescence of fine drops could be achieved via electrowetting effects. However, the coalesced droplets were trapped inside the coalescer device. That was detected by the droplet size distributions. The suggestions on the coalescer are as the following

- Run experiments with steady state inlet drop size distribution
- Test the coalescer device in conjunction with other filters to be used as a pre-coalescing device for enhancing the main filter performance.
- Modify the coalescer to account for drainage mechanism.
REFERENCES


121. V. Kumar, N. N. Sharma, SU-8 as Hydrophobic and Dielectric Thin Film in Electrowetting-on- Dielectric based Microfluidics Device, J. Nanotechnol. 2012, 6 (2012).


The Critical Path Method was used as a project management tool. The CPM was helpful in identifying the major tasks that should be conducted to finish the major tasks in PhD study. The CPM was developing over the course of study. The CPM is shown in Figure A.1.

Figure A.1 CPM. The important tasks in the research project.
APPENDIX B

PLEXIGLAS HOLDER DESIGNS AND COALESKER DESIGN

Plexiglas was used in many experiments, sometimes as holders and as containers in other times. For the electrode holders, the drawing is shown in Figure B.1.

Figure B.1 Top and side view drawing of the Plexiglas electrode holder. The Coalescer consisted of three parts, a rod and tube stainless steel parts and a Plexiglas base and cover. The drawing of these parts is presented in Figures B.2 and B.3.
Figure B.2 drawing of the coalescer.
Figure B.3 Top view of the Plexiglas cover.
APPENDIX C

DERIVING THE EXPRESSION FOR PREDICTING COALESCENCE ON HYDROPHOBIC SURFACES BY ELECTROWETTING

The drop volume is fixed when the droplet changes its contact angle on the same surface. The droplet is in the size range where surface tension dominates. By considering the geometry of the drop. The drop consists of hemispherical part and conical pert was well as a sectional part. Consider the drop shown in Figure 5.

![Figure C.1 schematic diagram of water droplet on a hydrophobic surface.](image)
The volume of the drop can be found by the following expression

\[ V_{\text{Drop}} = V_{\text{sphere}} + V_{\text{section}} + V_{\text{cone}} \]  \hspace{1cm} (C1.1)

\[ V_{\text{sphere}} = \frac{4}{3} \pi R^3 \]  \hspace{1cm} (C1.2)

\[ V_{\text{section}} = \frac{2}{3} \pi R^3 \cos \theta^\wedge \]  \hspace{1cm} (C1.3)

\[ V_{\text{cone}} = \frac{\pi}{3} a^2 h \]  \hspace{1cm} (C1.4)

By substituting C1.2 through C1.4 in (C1.1) and simplifying one can arrive to the following expression

\[ V_{\text{Drop}} = \frac{2}{3} R^3 (1 + \cos \theta^\wedge) + \frac{\pi}{3} a^2 h \]  \hspace{1cm} (C1.5)

where

\[ \theta^\wedge = \pi - \theta \quad \text{and} \quad h = -\frac{\cos \theta}{\sin \theta} \]  \hspace{1cm} (C1.6)

By substituting (C1.6) in (C1.5) and simplifying, one can arrive to the following expression
The above expression can be used to find the drop base radius as a function of
the measured contact angle and the drop volume.
APPENDIX D

VOLTAGE CALIBRATION AND RELAY POWER SWITCH

The data acquisition system consisted of a microprocessor to convert the analog signal to digitized bits displayed in the computer. The digitized bits range was 0 to 1023 bits. Calibration curves were produced by setting the voltage in the power supply to known voltages ranging from 0-600 VDC. MATLAB outputs are shown in the figures 6 and 7.

![Figure D.1 Data acquisition system output for the 600 VDC.](image)
Figures D.1 and D.2 show the outputs from the data acquisition system for the cases 550 VDC and 600 VDC. Similar curves were obtained for the voltages 0, 50, 100, 150, 200, 250, 300, 450 and 500 VDC. The calibration curve for converting the bits into the voltages is shown in Figure D.3.
The relay power switch had knobs for programming. The knobs were used to program the voltage output supply to the electrowetting experiments. The relay provides the preset power (or cuts) to the electrowetting experiments according to the programmed sequence. The relay works based on internal mechanical switches that execute based on the programmed sequence. The programming panel is shown in Figure D.4.
Figure D.4 Relay power switch panel. By using the panel, the voltage was programmed to be executed in a sudden step change mode.