

APPLICATION OF EWOD IN POROUS MICRO-MODELS

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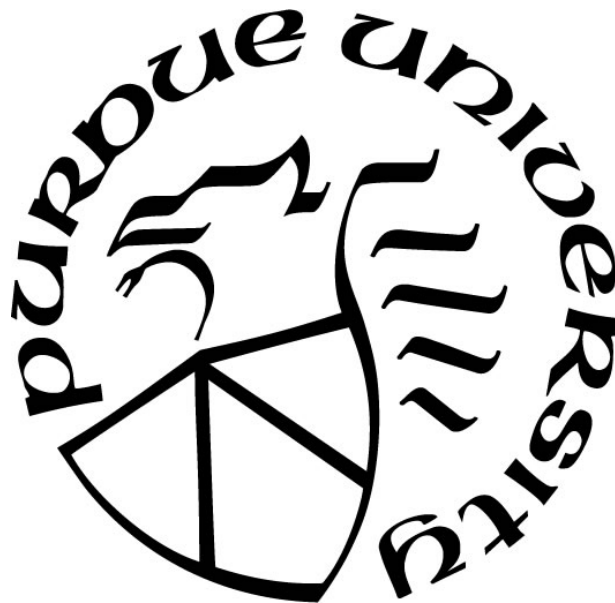
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To my wife for her love and support.
To my parents for their encouragement and patience.

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ABSTRACT

Single phase immiscible fluid flow in porous media is often described by Darcy's law. However, in two-phase or multi-phase conditions, the properties of porous medium rely on the saturation of each phase. One of the constitutive equations, the relationship between capillary pressure and saturation, exhibits hysteresis property. To accurately describe two-phase immiscible fluid in porous media, some researchers used interfacial area per volume (IAV) as an additional variable. Previous experiments were done by other experimenters to support the uniqueness of IAV in capillary pressure – saturation hysteresis relationship by externally changing the capillary pressure.

A technique called Electro-Wetting On Dielectric (EWOD) was developed for sealed micro-models to examine the saturation-pressure relationship by internally manipulating the saturation which in turns affects IAV. Single-plate EWOD samples were used to select material properties and experimental parameters. These experiments found that Poly-Di-Methyl-Siloxane (PDMS) is a good dielectric material that enabled changes in the contact angle between a droplet and PDMS from $\sim 120^\circ$ (non-wetting) to $\sim 50^\circ$ (wetting). Double-plate EWOD was used to demonstrate that discrete electrodes (with PDMS as dielectric on both plates) enabled the transportation and merging of droplet(s).

A novel method was developed to incorporate EWOD into a wedge-shaped PDMS micro-model. Imbibition and drainage scans of the capillary pressure – saturation relationship (P_c - S) were performed in the channel with and without voltage. The drainage curves differed significantly between the two conditions, while the imbibition curves were similar with and without voltage. The total energy for P_c - S decreased by 70 nJ with the application of EWOD with most of difference arising from a 20 Pa decrease in pressure for the same saturation condition during drainage.

Studies were also performed to examine the amount of energy associated with depinning of fluid interfaces. A 5-step wedge-shaped micro-model with EWOD was fabricated to increase the probability of pinning during an experiment. The amount of energy released as a fluid depinned was observed to be a function of capillary pressure. More energy was released at the 1st step for higher the pressures than lower pressures. The energy released from depinning at the first step in the channel ranged from 30 – 100 nJ for pressures from 70 to 100 Pa. The occurrence and

magnitude of additional depinnings along the step-shaped channel also depended on the pressure. Each successive depining released less energy.

Finally, experiments were performed to examine the range of EWOD in a sealed micro-model with discrete electrodes. When voltage was not applied directly on the fluid-fluid interface but on the solution, the voltage could still actuate the interface causing it to move and advance farther into a channel. The ability of the application of EWOD to drive fluid-fluid interfaces decreases with active electrode distance from the interface.

CHAPTER 1. INTRODUCTION

The study of immiscible flow in porous structures is important to a range of fields from environmental pollution [Jiang, *et al.*, 2007], to chemical reactions [Bureekaew, *et al.*, 2008], to energy science [Wood and Harris, 2008], and to nanoscience [Guilminot, *et al.*, 2008; Sarkar, *et al.*, 2007]. The complexity of pore networks and the effect of this complexity on two-phase flow have resulted in a wide range of theoretical models, computational approaches and experimental studies. Many of these investigations have focused on capillary pressure, which is a fundamental variable in the study of two-phase fluid flow in porous media.

Traditionally, capillary pressure is determined by externally increasing or decreasing fluid pressures to change the immiscible fluid saturation in a porous medium. The resulting saturation and interfacial area per volume (IAV) are then linked to the capillary pressure through constitutive equations [Gray and Miller, 2011] that describe the capillary pressure, P^c as a function of saturation, S , and IAV. Previous experiments [Chen, *et al.*, 2007; Liu, *et al.*, 2009; Liu, *et al.*, 2012] were focused on externally altering the pressure difference between the wetting and non-wetting phase to explore the uniqueness of IAV. The goal of this research is to discover whether externally measured pressures are sensitive to changes in distributions that arise from internal changes in contact angles and interfacial area per volume so as to test the robustness of the constitutive relation for P^c , S and IAV.

1.1 Porous Media

1.1.1 Darcy's Law

Single phase fluid flow in porous media is often described by Darcy's law [Darcy, 1856]. Darcy's law is an empirical relationship that is given by

$$Q = - \frac{kA\Delta P}{\mu L} \quad \text{Eq. (1.1)}$$

where Q represents the volumetric flow rate of a system with length L and cross-sectional area A , ΔP is the pressure difference across L , μ is the fluid viscosity, and k is the permeability, which is a property of the medium. A variety of forms have been derived for different applications such as 3D condition or in conditions where gravity needs to be taken into account.

Differential form

The differential form of Eq. (1,1) is given in equation 1.2:

$$q = -\frac{k}{\mu} \frac{dP}{dL} \quad \text{Eq. (1.2)}$$

where $q = Q/A$ is the Darcy flux and is defined as the volumetric flow rate per unit cross section area.

Vector form

The differential form for 3D applications is given in the vector form by

$$\vec{q} = -\vec{K} \vec{\nabla} P \quad \text{Eq. (1.3)}$$

where $\vec{q}$ is the Darcy flux vector, $\mathbf{k}$ and $\mathbf{K} = \mathbf{k}/\mu$, are permeability tensor and fluid conductivity, respectively, and $\vec{\nabla} P$ represents the gradient of pressure.

Gravitational effects

When gravitational effects are considered, the vector form acquires an additional term:

$$\vec{q} = -\vec{K}(\vec{\nabla} P - \rho \vec{g}) \quad \text{Eq. (1.4)}$$

where $\vec{g}$ is gravitational acceleration and ρ is the fluid density.

Eq. (1.1) – (1.4) serve as the basis for equations for describing systems with two immiscible phases.

1.1.2 Two phases condition, number of variable increases

A modified form of Darcy's law is used to study two-phase immiscible flow [Bear, 1972]. For immiscible fluids the two phases are often named wetting and non-wetting phase, respectively. Figure 1.1 shows a cross section of two-phase immiscible flow:

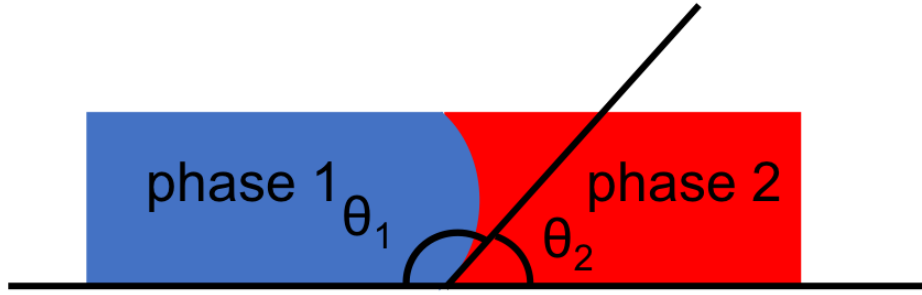


Figure 1- 1 A cross section of two immiscible phases. Phase 1 (Blue) is the non-wetting phase with a contact angle θ_1 that is greater than 90° , and phase 2 (Red) is the wetting phase and the contact angle θ_2 is less than 90° .

In Figure 1.1, phase 1 (blue) is the non-wetting phase. By definition, the non-wetting phase has a contact angle greater than 90° . Phase 2 is the wetting phase with a contact angle less than 90° . Darcy's law differs for each fluid phase and is given by

$$\vec{q}^w = -\frac{k k_r^w}{\mu^w} \nabla P^w \quad \text{Eq. (1.5)}$$

and

$$\vec{q}^n = -\frac{k k_r^n}{\mu^n} \nabla P^n \quad \text{Eq. (1.6)}$$

where the superscripts w and n, correspond to the wetting and non-wetting phase, respectively, and k_r is the relative permeability. One of two constitutive equations [Bear, 1972] that link relative permeability to saturation is

$$k_r^w = k_r^w(S^w) \quad \text{Eq. (1.7)}$$

where the definition of saturation is the fluid phase volume divided by the total pore volume of a porous medium. For an immiscible two-phase system, the sum of saturations of wetting and non-wetting phase is equal to 1:

$$S^w + S^n = 1. \quad \text{Eq. (1.8)}$$

If relative permeability exhibited a simple relationship with saturation, Darcy's law would still be applicable to immiscible two-phase systems. However, the value of relative permeability, k_r , depends also on whether imbibition or drainage takes place which can lead to hysteresis in the $k_r - S$ relationship (Figure 1.2). Imbibition means the displacement of a non-wetting fluid by a

wetting fluid, while the drainage means the displacement of a wetting fluid by a non-wetting fluid. The relationship between k_r and S also depends on the displacement history. Figure 1.2 shows the relationship between relative permeability and saturation of the wetting phase. This hysteretic relationship reveals that it requires additional variables to describe a two-phase system.

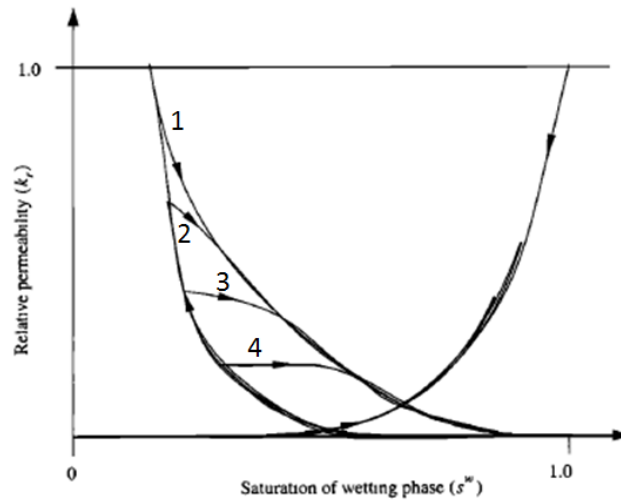


Figure 1- 2 Hysteretic relation of relative permeability and saturation of wetting phase. Relative permeability not only depends on saturation but also relates to displacement history. Different paths (1, 2, 3, 4) of imbibition yield different relationships between

1.1.3 Capillary Pressure

The other constitutive equation for modified Darcy's law relates capillary pressure, P^c to saturation S :

$$P^c = P^c(S^w). \quad \text{Eq. (1.9)}$$

This is also a hysteretic relationship as shown in Figure 1.3 [Bear, 1972; Muccino, *et al.*, 1998; Dullien, 1992; Reeves and Celia, 1996].

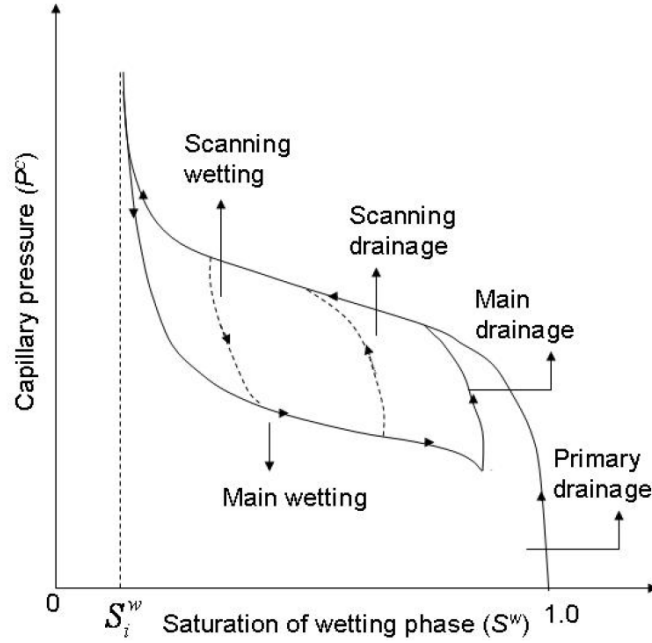


Figure 1- 3 A diagram of capillary pressure based on saturation of wetting phase starting from a fully wets saturation condition ($S_i^w=1.0$) [Bear, 1972; Muccino, *et al.*, 1998; Dullien, 1992; Reeves and Celia, 1996].

Capillary pressure is an important variable because it directly affects the saturation as well as the distribution of fluid phases. The definition of capillary pressure is given by:

$$P^c = \gamma^{wn} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad \text{Eq. (1.10)}$$

where γ^{wn} represents the interfacial tension between the wetting and non-wetting phases. R_1 and R_2 are the principal radii of curvature of the interface. We have

$$\left(\frac{1}{R_1} + \frac{1}{R_2} \right) = J \quad \text{Eq. (1.11)}$$

which is the mean curvature of the interface.

At equilibrium, capillary pressure is also determined as:

$$P_m^c = P^n - P^w \quad \text{Eq. (1.12)}$$

where P^n and P^w are the pressures of the non-wetting and wetting phases, respectively, P_m^c is the measured capillary pressure. This equation is only valid at equilibrium.

1.1.4 Interfacial Area per Volume (IAV)

Figure 1.3 shows capillary pressure as a function of wetting phase saturation. Note, that the P_c - S relationship is not a single-valued function. Figure 1.4 shows two images of the same micro-model containing a wetting phase decane and a non-wetting phase nitrogen. Though the saturations are the same, P_c and the fluid distribution differ.

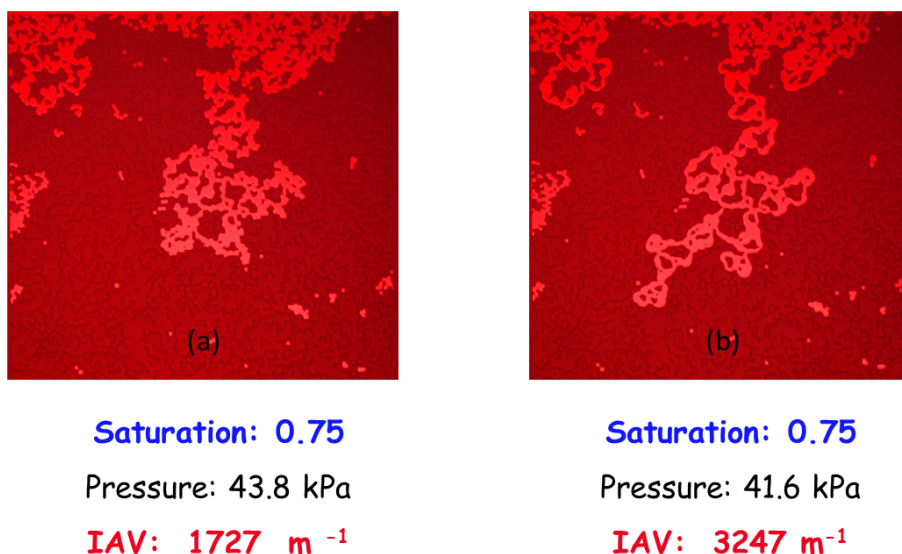


Figure 1- 4 Two conditions of the same sample of porous media. Condition (a) has saturation 0.75 and capillary pressure 43.8 kPa. Condition (b) has saturation 0.75 and capillary pressure 41.6 kPa.

When the capillary pressures are the same (Figure 1.5), the saturation and fluid distribution is observed to vary.

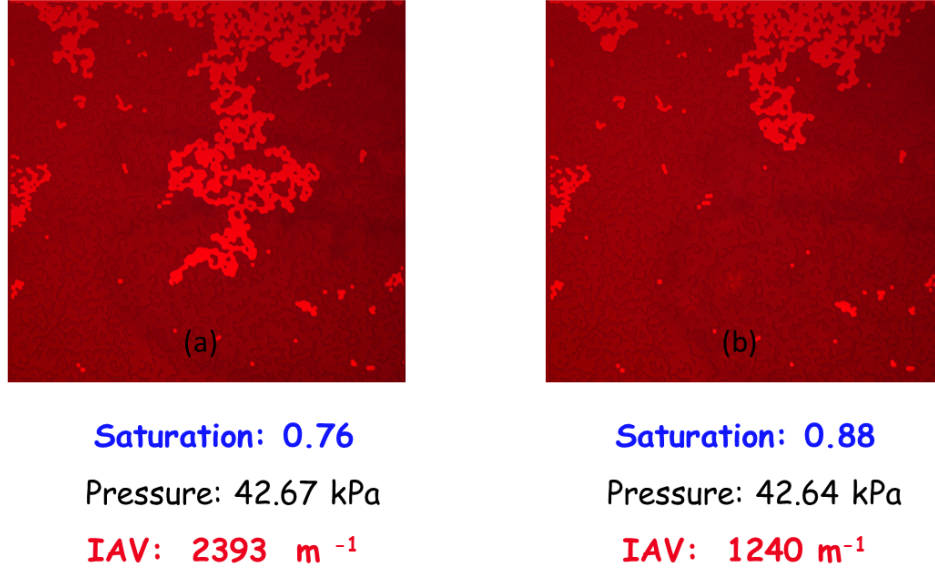


Figure 1- 5 Two conditions of the same sample of porous media. Condition (a) has saturation 0.76 and capillary pressure 42.67 kPa. Condition (b) has saturation 0.88 and capillary pressure 42.64 kPa.

This is an indication that additional variables are needed to fully determine two-phase immiscible fluid conditions.

Based upon thermodynamic methods and experimental observations [Cheng, *et al.*, 2004; Chen, *et al.*, 2007; Pyrak-Nolte, *et al.*, 2008; Liu, *et al.*, 2009; Liu, *et al.*, 2012], a new variable—interfacial area per volume (IAV) was proposed [Gray, 1999; Gray and Hassanizadeh, 1989; Hassanizadeh and Gray, 1990; Gray and Hassanizadeh, 1991; Muccino, *et al.*, 1998]. The definition of IAV is the interfacial area divided by the pore volume:

$$IAV = \frac{A_{\text{interface}}}{V_{\text{pore}}}. \quad \text{Eq. (1.13)}$$

In a two-phase fluid system, there are three IAVs, namely IAV_{ws} , IAV_{ns} and IAV_{wn} , for solid-wetting phase, solid – non-wetting phase and wetting – non-wetting phase interface, respectively. The two-phase system yields:

$$IAV_{ws} + IAV_{ns} = A_{\text{tot}}/V_{\text{pore}} \quad \text{Eq. (1.14)}$$

which is the total interfacial area per volume for this system. This variable, thus, describes the phase distribution of a system. Large non-wetting IAV indicates fine porous structure and vice versa.

Different experimental methods have been applied to measure IAVs for natural and artificial porous media. Packer, et al. and Zhang, et al. used nuclear magnetic resonance imaging (MRI) [Packer, et al., 1998; Zhang, et al., 2002]. X-ray computed micro-tomography and synchrotron-based X-ray micro-tomography were also applied [Brusseau, et al., 2007; Brusseau, et al., 2008; Culligan, et al., 2004; Culligan, et al., 2006]. Montemagno and Gray used photoluminescent volumetric imaging [Montemagno and Gray, 1995].

A first study of IAV focused on the uniqueness of this variable. Figure 1.6 [Cheng, et al., 2004] shows IAV_{nw} as a function of capillary pressure and saturation from a micro-model system where the fluids were nitrogen and decane. The result yielded that within a 5% error, IAV_{nw} is a unique variable.

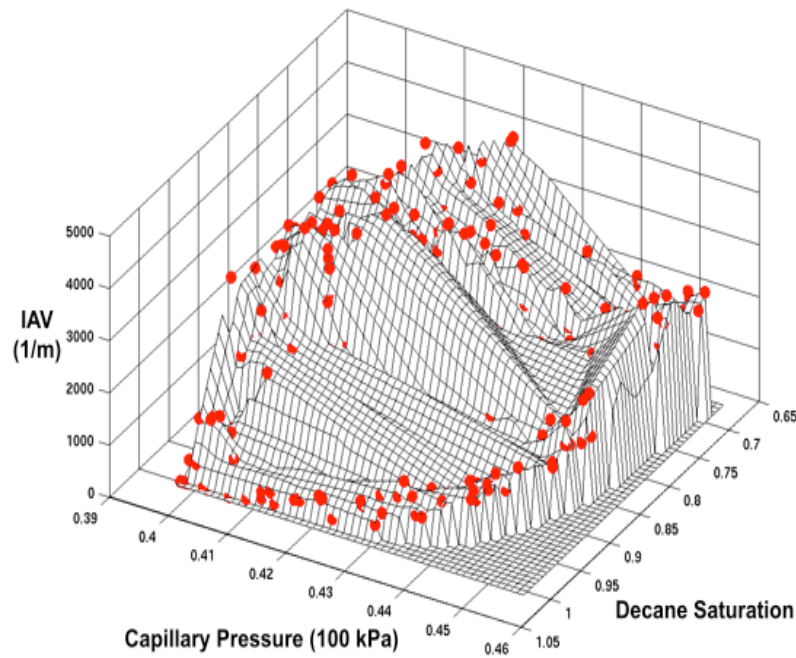


Figure 1- 6 IAV_{nw} as a function of pressures and saturation [Cheng, et al., 2004]. The surface is unique within 5% error.

Chen, et al. [Chen, et al., 2007] pointed out that the results from Cheng, et al., in Figure 1.6 were based on the analysis of a single surface and did not compare imbibition and drainage

surfaces. Chen used micro-models and showed that the differences between imbibition and drainage surfaces were within 10-15%.

1.2 EWOD (Electro-Wetting On Dielectric)

Previous experimental studies on IAV_{nw} manipulated the external pressure of each fluid phase [Cheng, *et al.*, 2004; Chen, *et al.*, 2007; Liu, *et al.*, 2009; Liu, *et al.*, 2012]. To verify the uniqueness of IAV_{nw} , a special technique is required to internally alter the IAV_{nw} or saturation to study the corresponding change in capillary pressure.

Contact angles and fluid distributions can be manipulated by using an electro-kinetic technique referred to as EWOD (Electro-Wetting On Dielectric). When a potential difference exists across an aqueous droplet, the droplet changes its shape. This phenomenon is called EWOD and occurs because the wettability of the insulator/liquid interface is altered by the application of voltage. As the applied voltage increases, the wettability of the insulator layer increases and the contact angle decreases. The interface can change from hydrophobic (non-wetting) to hydrophilic (wetting). Basic applications of EWOD (including the manipulations of droplets) are: dispensing [Ren, *et al.*, 2003; Cho, *et al.*, 2003], transporting [Cho, *et al.*, 2003], splitting [Cho, *et al.*, 2001; Cho, *et al.*, 2003; Zhao and Cho, 2006] and merging fluids [Cho, *et al.*, 2003; Zhao and Cho, 2006]. The possibility of applying EWOD to create tunable lenses has also been studied. [Berge and Peseux, 2000; Pollack, *et al.*, 2000; Krupenkin, *et al.*, 2003]

1.2.1 Contact Angle

In an EWOD set-up, three immiscible phases are in contact as shown in Figure 1.7.

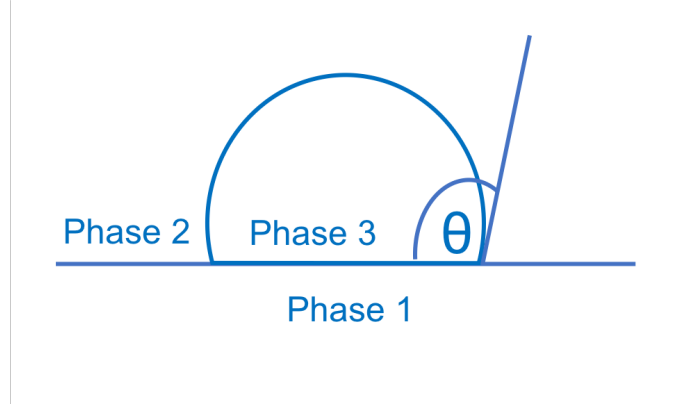


Figure 1- 7 Three phases (phase 1 = s, phase 2 = v, phase 3 = l, s = solid, v = vapor, l = liquid) for a droplet to on a solid surface. [Herberth, 2006] θ is the contact angle between s and l.

The three phases are a solid phase, s (dielectric layer), a vapor phase, v (air) and a liquid phase, l (droplet). Three interfaces exist among the three phases: vs, ls and vl. Each interface has an interfacial energy γ_{ij} . Here, i and j correspond to two different phases among s, v, l. Interfacial energy differs from surface energy. The definition of interfacial energy is, the amount of energy G needed under reversible and isothermal conditions, to increase the surface A of an interface at constant volume:

$$\gamma_{ij} = \left. \frac{dG}{dA} \right|_{TV}. \quad \text{Eq. (1.15)}$$

The contact angle can be calculated through a thermodynamic variational approach [Verheijen and Prins, 1999]. For example, Figure 1.8 shows a change in contact angle from θ to θ' for a very small displacement of area dA near equilibrium conditions.

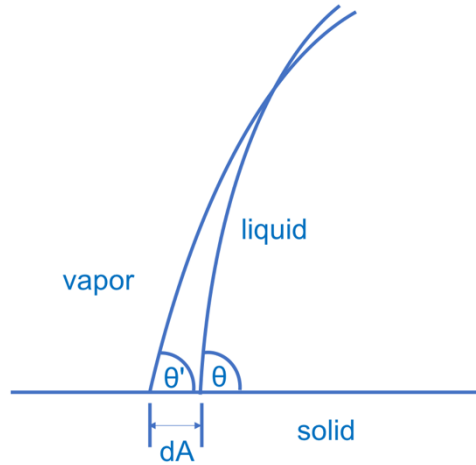


Figure 1- 8 By changing a very small displacement with an aerial difference dA , the contact angel changes from θ to θ' .

The variation of free energy is composed of three parts:

$$dG = \gamma_{sl}dA - \gamma_{sv}dA + \gamma_{lv}dA \cos \theta. \quad \text{Eq. (1.16)}$$

In an equilibrium state, the total free energy is minimized, which leads to:

$$\frac{dG}{dA} = 0 \quad \text{Eq. (1.17)}$$

$$\frac{dG}{dA} = 0 = \gamma_{sl} - \gamma_{sv} + \gamma_{lv} \cos \theta. \quad \text{Eq. (1.18)}$$

This yields Young's equation:

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad \text{Eq. (1.19)}$$

which describes the relationship among the interfacial energies and the contact angles. Data of interfacial energies of these phases can be easily determined (material properties).

Theoretically, the contact angle between a droplet and a uniform layer of material is derived. However, the measured contact angle in an experiment is highly dependent on the roughness of the solid surface and manner of placing a droplet. If a small amount of liquid is added to the droplet, the contact angle line is still pinned because the roughness stops it from moving, which causes an increase in contact angle. Instead, a small amount of liquid is removed from the droplet, the contact angle will decrease. So the surface has an advancing (maximal) contact angle θ_A and a receding (minimal) contact angle θ_R .

Young's equation corresponds to a perfectly flat surface. The relationship between the contact angle in Young's equation and θ_A and θ_R has been studied theoretically [Tadmor, 2004] and experimentally [Chibowski and Terpilowski, 2008] and determined to be:

$$\theta = \cos^{-1}\left(\frac{r_A \cos \theta_A + r_R \cos \theta_R}{r_A + r_R}\right) \quad \text{Eq. (1.20)}$$

where

$$r_A = \left(\frac{\sin^3 \theta_A}{2 - 3 \cos \theta_A + \cos^3 \theta_A}\right)^{1/3}$$

and

$$r_R = \left(\frac{\sin^3 \theta_R}{2 - 3 \cos \theta_R + \cos^3 \theta_R}\right)^{1/3}.$$

1.2.2 Thermodynamic Approach After Applying Voltage

Next, the effect of an applied voltage on the expression of total free energy (Eq. (1.17)) is presented. Application of a voltage adds two additional terms, dU and dW to this formula. U is the energy required to produce an electric field between the droplet and a counter ground electrode. W is the energy associated with the external applied voltage source. Putting a d before them means taking derivation. Under this condition, dW is negative and $dW = -2dU$. The total free energy then becomes:

$$dG = \gamma_{sl}dA - \gamma_{sv}dA + \gamma_{lv}dA \cos \theta + dU + dW \quad \text{Eq. (1.21)}$$

$$dG = \gamma_{sl}dA - \gamma_{sv}dA + \gamma_{lv}dA \cos \theta - dU. \quad \text{Eq. (1.22)}$$

W is determined from the following equations:

$$-W = CV^2 = \epsilon_0 \epsilon_r \frac{A}{d} V^2. \quad \text{Eq. (1.23)}$$

$$-\frac{W}{A} = \frac{\epsilon_0 \epsilon_r}{d} V^2. \quad \text{Eq. (1.24)}$$

$$-\frac{dW}{dA} = \frac{\epsilon_0 \epsilon_r}{d} V^2. \quad \text{Eq. (1.25)}$$

Then Eq. (1.22) becomes:

$$dG = \gamma_{sl}dA - \gamma_{sv}dA + \gamma_{lv}dA \cos \theta - \frac{1}{2} \frac{\epsilon_0 \epsilon_r}{d} V^2 dA. \quad \text{Eq. (1.26)}$$

Here, C and A are the capacitance and area of the dielectric layer, respectively. V is the applied voltage, ϵ_0 and ϵ_r are the vacuum permittivity and the dielectric constant of the dielectric layer, respectively. At equilibrium, the total free energy is minimized:

$$\frac{dG}{dA} = 0 = \gamma_{sl} - \gamma_{sv} + \gamma_{lv} \cos \theta - \frac{1}{2} \frac{\epsilon_0 \epsilon_r}{d} V^2 \quad \text{Eq. (1.27)}$$

which yields the Young-Lippman equation:

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} + \frac{1}{2} \frac{\epsilon_0 \epsilon_r}{\gamma_{lv} d} V^2. \quad \text{Eq. (1.28)}$$

Eq. (1.28) relates the contact angle to an externally applied voltage. However, this equation is not valid for all voltages since $\cos 0^\circ = 1$, i.e. a contact angle of zero is usually not achievable on most surfaces because of material properties and surface roughness. At high voltage, the contact angle saturates. This will be discussed in section 1.2.5.

1.2.3 Electromechanical Approach

The Korteweg-Helmholtz body force density is often used to understand how the mechanical force affects the reduction of contact angle, [Mugele and Baret, 2005]. The Korteweg-Helmholtz body force is given by:

$$\vec{f}_k = \rho_f \vec{E} - \frac{\epsilon_0}{2} E^2 \nabla \epsilon_r + \nabla \left[\frac{\epsilon_0}{2} E^2 \frac{\partial \epsilon_r}{\partial \rho} \rho \right] \quad \text{Eq. (1.29)}$$

where ϵ_r and ρ are the dielectric constant and mass density of the liquid, respectively. The last term is called electrostriction and can be neglected in EWOD situation because of uniform density distribution. Thus, the Maxwell tensor from Eq. 1.29 can be expressed by:

$$T_{ik} = \epsilon_0 \epsilon_r \left(E_i E_k - \frac{1}{2} \delta_{ik} E^2 \right). \quad \text{Eq. (1.30)}$$

Here, the Kronecker delta function is δ_{ik} , $i, k = x, y, z$. If we consider a small volume dV at the liquid-vapor interface of EWOD system that is perfectly conductive (Figure 1.9), the tangential component of the surface electrical field vanishes. The normal component of the force is related to the surface charge density via:

$$\sigma_s = \epsilon_0 \vec{E} \cdot \vec{n} \quad \text{Eq. (1.31)}$$

The force can be calculated by integrating the Maxwell stress tensor over the closed surface vector:

$$F_i = \oint T_{ik} n_k dA \quad \text{Eq. (1.32)}$$

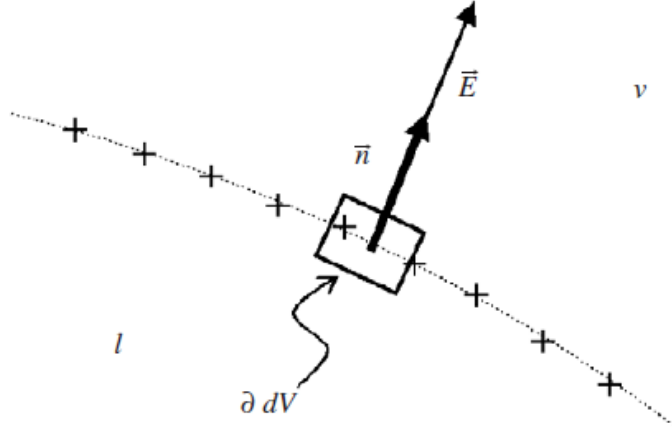


Figure 1- 9 Force acting on a small volume of dV . The area marked with “+” is the place for surface integral [Mugele and Baret, 2005].

Substitute Eq 1.30 into Eq 1.32, we have:

$$F_i = \oint \epsilon_0 \epsilon_r \left(E_i E_k - \frac{1}{2} \delta_{ik} E^2 \right) \cdot n_k dA \quad \text{Eq. (1.33)}$$

$$F_i = \oint \left(\epsilon_0 \epsilon_r E_i E_k n_k - \frac{1}{2} \epsilon_0 \epsilon_r \delta_{ik} n_k E^2 \right) dA \quad \text{Eq. (1.34)}$$

$$F_i = \oint \left(\epsilon_0 \epsilon_r E_i \vec{E} \cdot \vec{n} - \frac{1}{2} \epsilon_0 \epsilon_r n_i E^2 \right) dA \quad \text{Eq. (1.35)}$$

Thus,

$$\frac{d\vec{F}}{dA} = \frac{1}{2} \sigma_s \vec{E} \quad \text{Eq. (1.36)}$$

By using a conformal mapping method first proposed by Vallet et al. [Vallet et al., 1999], Kang [Kang, 2002] calculated the force on the liquid/vapor interface as:

$$F_x = \frac{\epsilon_0 \epsilon_r V^2}{2d} \quad \text{Eq. (1.37)}$$

$$F_y = \frac{\epsilon_0 \epsilon_r V^2}{2d} \cot \theta \quad \text{Eq. (1.38)}$$

Here, x is the direction parallel to liquid/solid interface and y is normal to this interface. This calculation yields the same result as Eq. (1.28) in section 1.2.2.

1.2.4 Relaxation Time and Debye Screening Length

The definition of the relaxation time for a RC system is determined by:

$$\tau = RC \quad \text{Eq. (1.39)}$$

where R is the total resistance and C is the total capacitance. A single-plate EWOD system is equivalent to an AC circuit (see Figure 1.10) [Klarman, *et al.*, 2011; Nanayakkara and Armstrong, 2011].

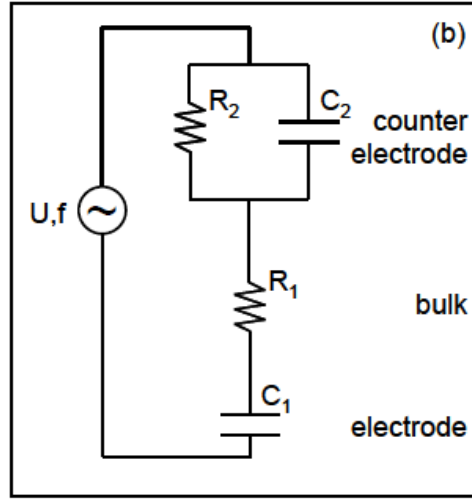


Figure 1- 10 Equivalent AC circuit of an EWOD setup. The substrate/liquid interface is treated as a capacitor C_1 , the bulk liquid drop is treated as a resistor R_1 while the counter electrode/liquid interface is equal to a capacitor C_2 . R_2 represents the Faradic charge transfer processes.

In their model, $R_1 \gg R_2$. Thus we take $R = R_1$. As for the capacitance, it is the sum of C_1 and C_2 . A parallel-plate capacitor model [Monroe, *et al.*, 2006] shows that

$$C \cong \epsilon_0 A \left(\frac{d}{\epsilon_r} + \frac{\lambda_D}{\epsilon_l} \right)^{-1} \quad \text{Eq. (1.40)}$$

where A is the substrate area that is covered by the liquid droplet, λ_D is the Debye screening length and ϵ_l is the dielectric constant of the liquid. For a charged solid surface in contact with a liquid, the definition of Debye screening length is (from solving the Poisson equation) [Nelson and Kim, 2012]:

$$\nabla^2 \psi = \frac{d^2 \psi}{dy^2} = \frac{-\rho_E}{\epsilon} \quad \text{Eq. (1.41)}$$

where Ψ is the potential function, y is normal to the solid where $y = 0$, ρ_E is the charge density and ϵ is the permittivity of the liquid. From Boltzmann statistics, the concentration n_i with a species i having valence z_i is:

$$n_i = n_{i\infty} \exp \left(-\frac{z_i e \psi}{k_B T} \right) \quad \text{Eq. (1.42)}$$

where e is the charge of an electron, $n_{i\infty}$ is the concentration of liquid far from the surface, k_B is the Boltzmann constant and T is the temperature. The charge density is given by:

$\rho_E = \sum z_i n_i e$, which yields:

$$\frac{d^2 \psi}{dy^2} = -\frac{e}{\epsilon} \sum_i z_i n_{i\infty} \exp \left(-\frac{z_i e \psi}{k_B T} \right) \quad \text{Eq. (1.43)}$$

If $z_i e \psi \ll k_B T$, then Eq. (1.43) becomes:

$$\frac{d^2 \psi}{dy^2} = \frac{1}{\lambda_D^2} \psi \quad \text{Eq. (1.44)}$$

with:

$$\lambda_D = \frac{1}{e} \left(\frac{\epsilon k_B T}{\sum_i z_i^2 n_{i\infty}} \right)^{1/2} \quad \text{Eq. (1.45)}$$

A symmetric electrolyte having liquid concentration of molarity M has a Debye length of

$$\lambda_d \approx 3 \times 10^{-10} |z|^{-1} M^{-1/2} \quad \text{Eq. (1.46)}$$

In conclusion, even for deionized water, the Debye length is $\sim 1 \mu\text{m}$. Based on the small value of Debye length, the capacitance of the system is approximated:

$$C \cong \frac{\epsilon_0 \epsilon_r}{d} A \quad \text{Eq. (1.47)}$$

Thus, from Eq. 1.33, with $R=l/\sigma_l A$, the dielectric relaxation time is:

$$\tau \approx \frac{\epsilon_0 \epsilon_r l}{\sigma_l d} \quad \text{Eq. (1.48)}$$

where l is the scale of droplet. For a system with $\epsilon_r = 3$, $l = 1 \text{ mm}$, $\sigma_l = 1 \text{ S/m}$ and $d = 20 \mu\text{m}$, $\tau \approx 1\text{e-9 s}$, which is a pretty small value.

For these parameters, the response to EWOD can be treated as an immediate response.

1.2.5 Saturation at Hight Voltage

As derived in section 1.2.2, the Young-Lippman equation yields a linear relationship between cosine of the contact angle ($\cos \theta$) and the square of the applied potential (V^2) in EWOD. As mentioned, this equation cannot always be true because when $V \rightarrow \infty, \cos \theta \rightarrow \infty$, which violates the domain of the cosine function. Experiments have observed contact angle saturation in EWOD [Vallet, et al., 1996; Welters and Fokkink, 1998; Vallet, et al., 1999; Mugele and Baret, 2005]. At relatively low voltage, contact angles are related to the applied voltages via Eq. (1.28). At high voltage, the contact angle decreases and asymptotes to a certain value known as the saturation contact angle, θ_{sat} . This phenomenon is illustrated in Figure 1.11.

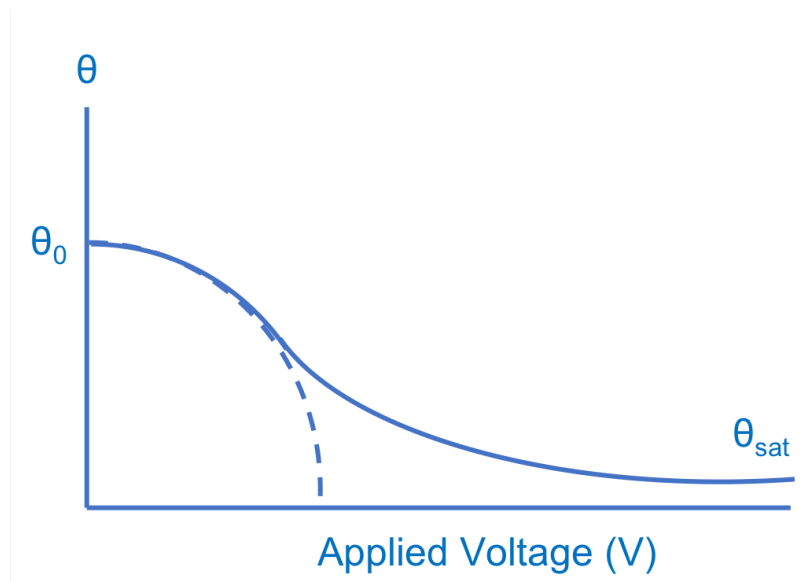


Figure 1- 11 The relation between contact angle and applied voltage. The dashed line matches Eq 1.27. While in real condition, at low voltage, the experimental results fit Eq 1.27 well. At high voltage, the contact angle approaches a constant value, θ_{sat} .

The origin of contact angle saturation, although observed multiple times in experiments, is still unsolved and no unified explanation has been proposed. Instead, several models have been put forward including trapping of charge, vapor ionization, zero interfacial tension,

electrohydrodynamic instability, local breakdown of the dielectric and reversed electrowetting. In the next sections, a brief description of these models is given.

1.2.5.1 Trapping of charge

In Figure 1.12, an additional layer of trapped charges develops in the dielectric material as the voltage increases [Verheijen and Prins, 1999]. Due to the existence of this trapped charge, a counter potential is created that lowers the effective potential.

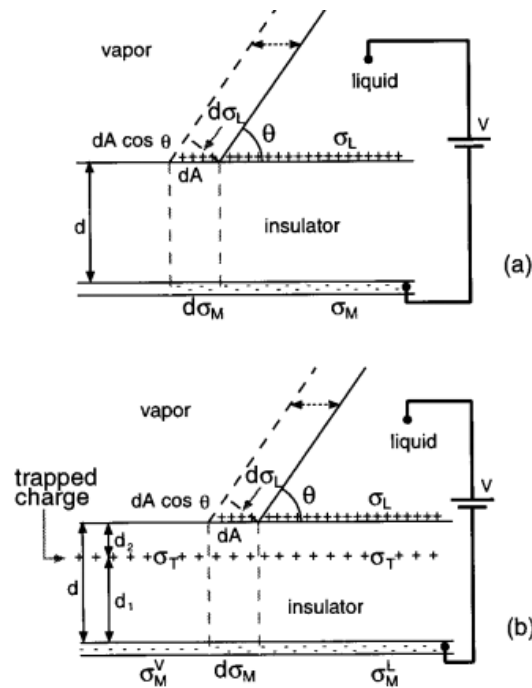


Figure 1- 12 Schematic diagram of trapped charge model [Verheijen and Prins, 1999]. (a) shows no trapped charges condition. (b) shows that when voltage goes high, a layer of trapped charge σ_T emerges within the dielectric layer, which lowers the effect of original charge σ_L .

Figure 1.13 shows a sketch of potential (a) and the electric field (b) in the dielectric layer beneath the liquid and the vapor phase.

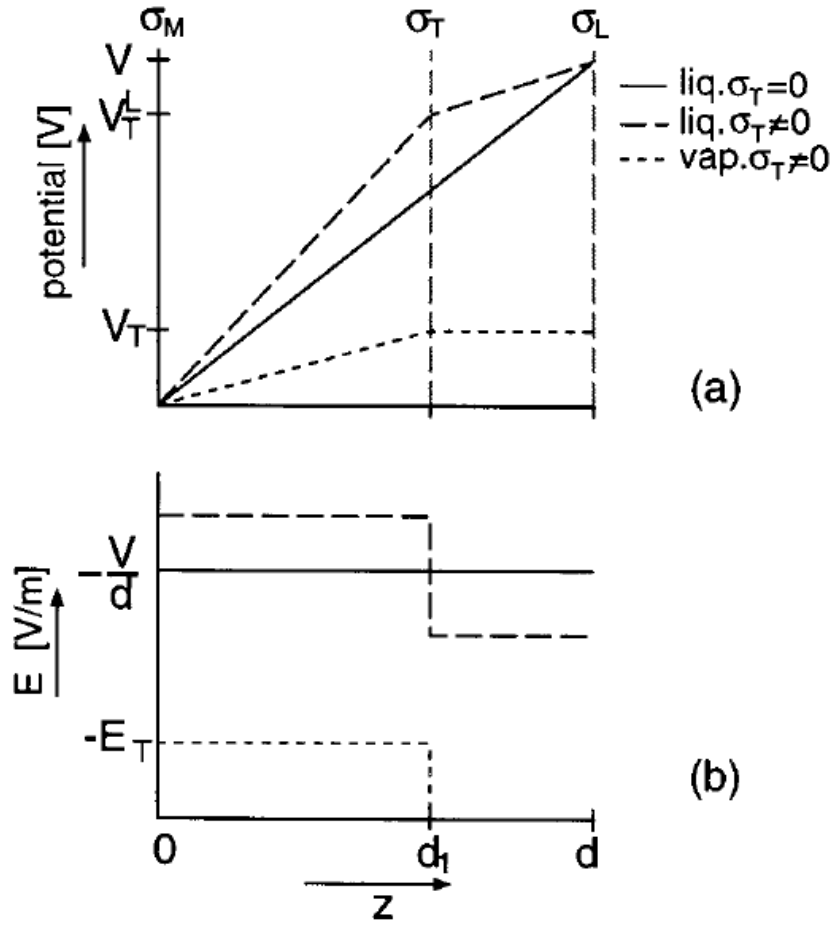


Figure 1- 13 A sketch of the voltage (a) and electric field (b) formed by trapped charge [Verheijen and Prins, 1999]. The solid line means no trapping charges condition. The long-dashed line corresponds to condition with trapping charges inside the dielectric. The short-dashed line is related to the condition with trapping charges beneath the vapor phase.

In Figure 1.13, if there is no trapping of charges, the potentials of two sides of the dielectric are 0 and V , respectively. If trapping charges of σ_T occurs beneath the liquid droplet with a distance of $d-d_1$, the potentials of the two sides of the dielectric are still 0 and V . But it's not a linear relationship. Due to the existence of the trapping charges inside, the electrical field has a larger value before the trapped charges then decreases. If the trapping charges are beneath the vapor phase, the potential beneath the droplet is not V .

This layer of trapped charges is removable when the applied voltage is reversed. As for this model, a modified equation based upon Eq. (1.27) was derived:

$$\cos \theta = \frac{\gamma_{sl} - \gamma_{sv}}{\gamma_{lv}} + \frac{1}{2} \frac{\epsilon_0 \epsilon_r}{\gamma_{lv} d} (V - V_T)^2. \quad \text{Eq. (1.49)}$$

In this model, V_T depends on the dielectric material. However, the value of the trapped voltage from theories was not found. Another weakness of this model is that it doesn't account for the use of AC voltage. Theoretically, there is no trapped charge under the condition of an AC source. However, for EWOD, we cannot conclude that saturation occurs for the same reason for both AC and DC.

1.2.5.2 Vapor ionization

Vallet et al. [Vallet, et al., 1999] observed in their experiments that luminescence emerged around the triple contact line (TCL) where all line phases are in contact when voltage exceeds the saturation voltage. Figure 1.14 & 1.15 show the side and top view of this phenomenon, respectively.

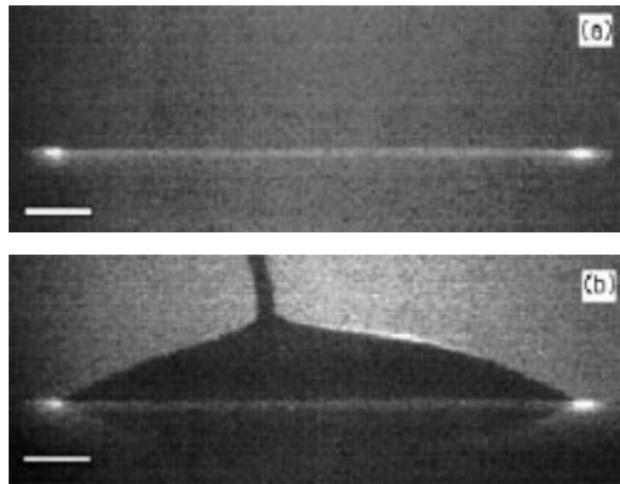


Figure 1- 14 Side views of images taken in saturation EWOD. [Vallet, et al., 1999] (a) With no light. (b) With a little light.

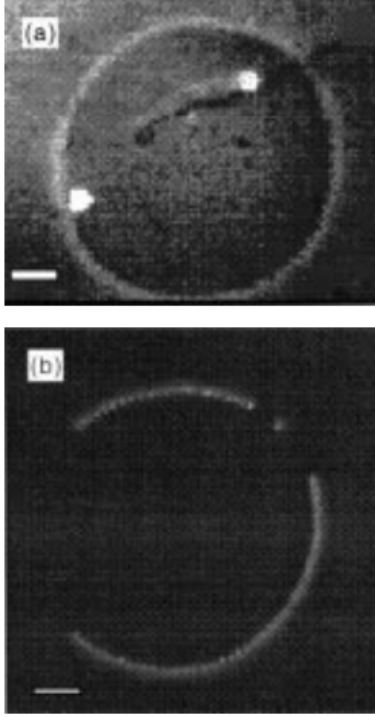


Figure 1- 15 Top views of images taken in saturation EWOD. [Vallet, *et al.*, 1999] (a) With a little light. (b) With no light.

They assumed that the luminescence was an indication of vapor ionization that resulted in EWOD saturation. In this hypothesis, because air is ionized, charges escape from the liquid/solid interface into the vapor phase. In the standard model (Eq. 1.28), air is assumed to be an insulator. The flow of charges in air weakens the effect of EWOD, leading to saturation. The dielectric breakdown of air is 3.0 MV/m, which makes this assumption possible.

1.2.5.3 Zero interfacial tension

The zero interfacial tension model [Peykov *et al.*, 2000] proposes that the solid-liquid interfacial tension is modified as the contact angle changes, that is:

$$\gamma_{sl} = \gamma_{sl}^0 + \Delta G. \quad \text{Eq. (1.50)}$$

For the stability of this interface, γ_{sl} should remain positive, which leads to saturation:

$$\cos \theta = \frac{\gamma_{sl}(\geq 0) - \gamma_{sv}}{\gamma_{lv}}. \quad \text{Eq. (1.51)}$$

However, this is only a theoretical model. No experimental evidence currently supports this hypothesis.

1.2.5.4 Electrohydrodynamic instability

Chevalott, et al. designed a series of complex experiments to verify previously proposed mechanisms to explain saturation [Chevalott, et al., 2011]. In their paper, the effects of dielectric thickness, interfacial tension, pH, ion type/size, solute/solvent interaction and DC/AC voltage on saturation were investigated. This paper is interesting because it didn't conclude the primary reason for saturation but eliminated several choices. In their experiments, they found that by applying AC voltage, EWOD has a lower saturation contact angle (Figure 1.16). Molarity affects the contact angle-voltage curve as well but not remarkably (Figure 1.17).

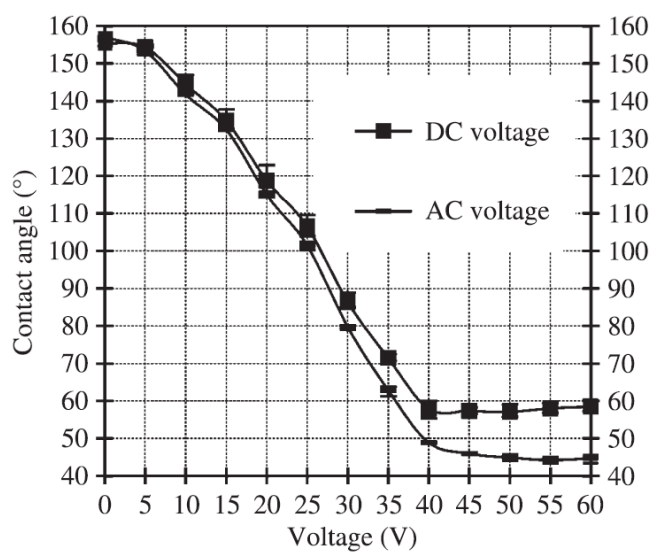


Figure 1- 16 The effect of DC/AC voltage on EWOD saturation. The AC frequency is 1kHz. In this figure, AC voltage gives lower saturation contact angle compared with DC voltage with all other conditions the same.

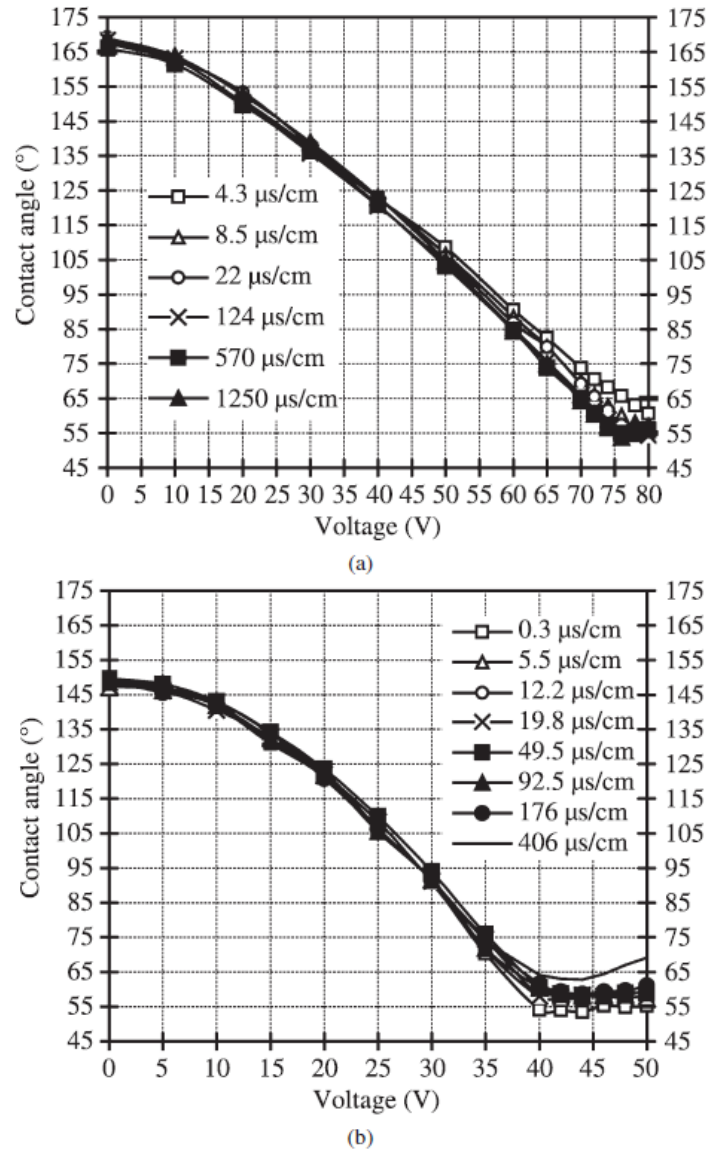


Figure 1- 17 The effect of conductivity on EWOD saturation for two different solvent (a). deionized water and (b). propylene carbonate. The contact angle shows a difference of 10° in (b).

1.2.6 Double-Plate EWOD and Pressure

With single-plate EWOD, it is relatively easy to alter the contact angle. However, my goal is to change the pressures of fluids in a micro-model. To achieve this, double-plate EWOD was utilized. A setup of a double-plate EWOD is shown in Figure 1.18. A droplet is placed in between a plate with discrete electrodes and a counter ground electrode. With this setup, by turning the electrodes on/off, a droplet can be manipulated to transport, merge, split. This phenomenon occurs

because of the production of a pressure difference across the drop. To analyze this, I start from Young-Laplace equation.

The Young-Laplace equation relates the capillary pressure between two fluid phases to the curvature of the vl interface. Young [Young, 1805] generalized the conception and Laplace [Laplace, 1807] derived an expression for the relationship, that is:

$$\Delta p = -\gamma \vec{\nabla} \cdot \hat{n} = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right). \quad \text{Eq. (1.52)}$$

Here, Δp is the pressure difference across the interface between two fluid phases, γ is the surface tension, $\hat{n}$ is the unit normal vector pointing out of the interface, R_1 and R_2 are the principle radii of curvature. When two immiscible fluids are between two plates or walls (Figure 1.18), the expression for capillary pressure is:

$$\Delta p = \Delta p_{\text{left}} - \Delta p_{\text{right}} \quad \text{Eq. (1.53)}$$

with:

$$\Delta p_{\text{left}} = -\frac{\gamma_{lv}}{d'} [(\cos \theta_{ll} + \cos \theta_{ul}) - p_{\text{inner}}] \quad \text{Eq. (1.54)}$$

and

$$\Delta p_{\text{right}} = -p_{\text{inner}} - \frac{\gamma_{lv}}{d'} [(\cos \theta_{lr} + \cos \theta_{ur})] \quad \text{Eq. (1.55)}$$

The expression for the pressure difference is:

$$\Delta p = \frac{\gamma_{lv}}{d'} [(\cos \theta_{lr} + \cos \theta_{ur}) - (\cos \theta_{ll} + \cos \theta_{ul})]. \quad \text{Eq. (1.56)}$$

Here, d' is the aperture between two plates, the first “l” or “u” corresponds to lower or upper, the second “l” or “r” relates to left or right.

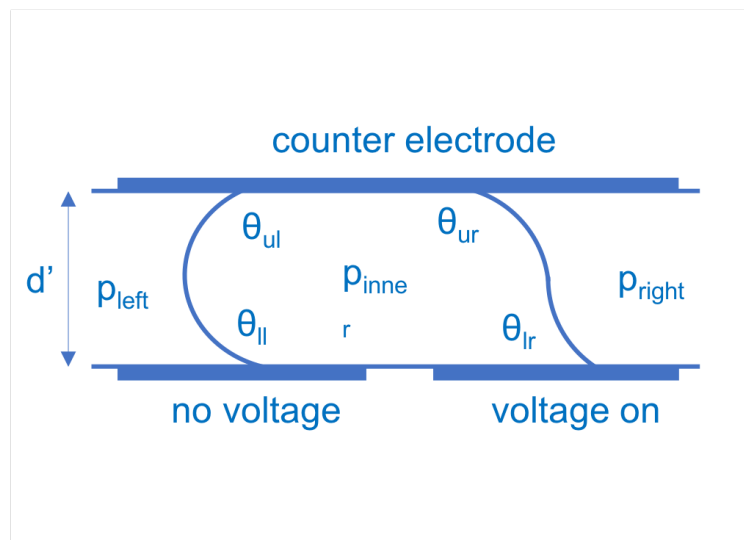


Figure 1- 18 Double-plate EWOD. A droplet is placed onto two separated electrodes controlled individually. It is covered by another counter electrode.

While applying a voltage on the right electrode with the left electrode off and substituting the expression for θ from eq. 1.28 into eq. 1.56 yields:

$$\Delta p = \frac{\gamma_{lv}}{d'} [(\cos \theta_{lr} - \cos \theta_{ll}) + (\cos \theta_{ur} - \cos \theta_{ul})] = \frac{\gamma_{lv}}{d'} \frac{1}{2} \frac{\epsilon_0 \epsilon_r}{\gamma_{lv} d} V^2 = \frac{\epsilon_0 \epsilon_r}{2 d d'} V^2 \quad \text{Eq. (1.57)}$$

Again, the contact angle still depends linearly on V^2 . Here V represents the pressure difference between the droplet and the lower electrodes. If we have a very thin layer of insulator on the upper plate, we can treat V as the applied voltage. The pressure difference will depend on the voltage and dielectric constant of the surface as well as on the thickness of the dielectric and aperture, i.e. distance between upper and lower surface.

To fulfill my research goal, I used EWOD methods to manipulate saturation and IAV_{nw} in micro-fluidic porous media. In section 1.3, background on micro-models is presented.

1.3 PDMS Mirco-Model

1.3.1 Micro-Models

Micro-models are transparent flow cells that enable direct visualization of fluid distributions. Transparent flow cells have been widely used for science and engineering research to study fluid behavior in porous media. In addition, artificial porous media overcome the difficulty of acquiring experiment data from real systems such as rock and soil which are opaque to most probes.

Micro-models have been made from a variety of materials. Fourar, et al. first used beads to build micro-models [Fourar, et al., 1993]. A single layer of 1-mm-diameter glass beads were glued on a 0.3-mm-thick layer of transparent epoxy cement on a surface (figure 1.19). Etching micro channels into glass [DetWiler, et al., 1999; Stewart and Fogler, 2002; Wan and Wilson, 1994] or silicon [Baumann and Werth, 2004; Keller, et al., 1997; Keller and Sirivithayapakorn, 2004] substrates is another widely used approach. Figure 1.21 shows a glass micro-model with hexagonal networks. Figure 1.21 shows a composite image and a scanning electron microscope image of micro-models built in silicon. Photoresist based approaches have been also used to form channels and pore networks such as in Figure 1.22 [Chen, et al., 2007; Cheng, et al., 2004; Pyrak-

Nolte, et al., 2008] and Figure 1.23 [*Liu, et al., 2010*]. PDMS micro-models (which are used in this study) will be discussed in section 1.3.2.

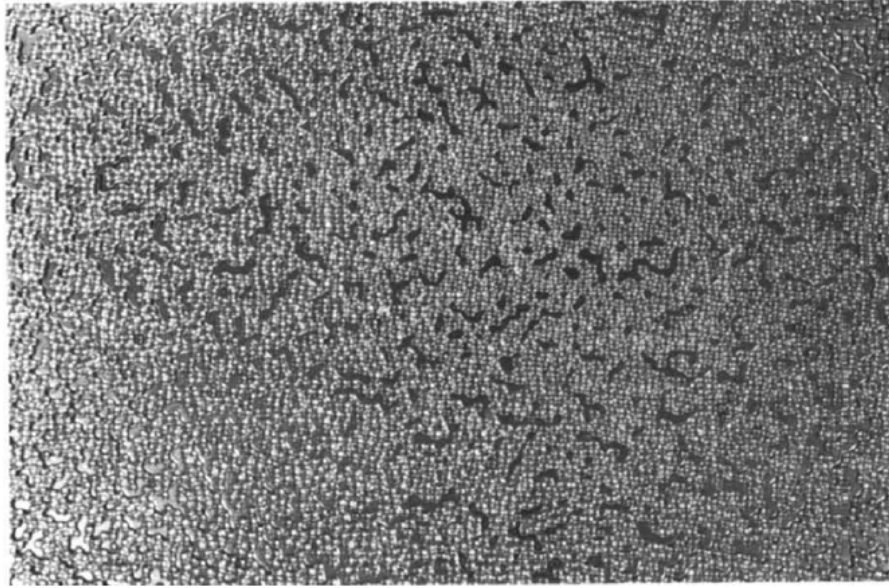


Figure 1- 19 Micro-model built with beads [*Fourar, et al., 1993*]. This is a single layer beads with a thickness of ~ 1 mm.

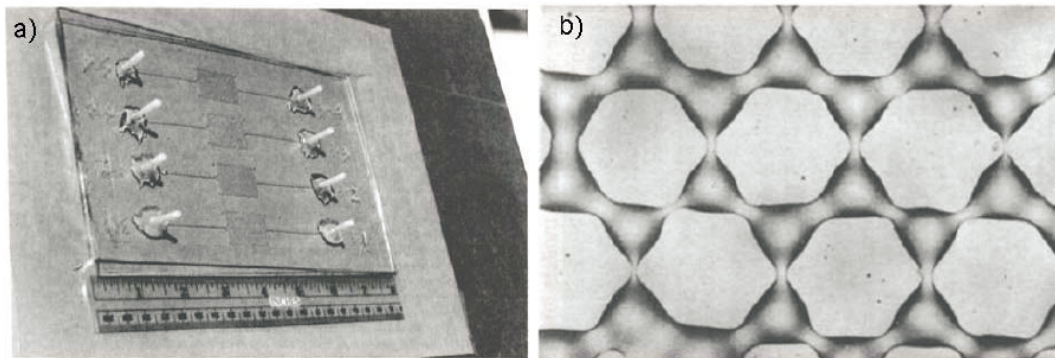


Figure 1- 20 Micro-model built with glasses [*Wan and Wilson, 1994*]. (a) Appearance of a four-network micro-model. (b) Hexagonal pore network of this micro-model. It has 1116 pore bodies in this model. Pore bodies are sized $300\text{ }\mu\text{m}$ while throats are sized $20\text{-}100\text{ }\mu\text{m}$.

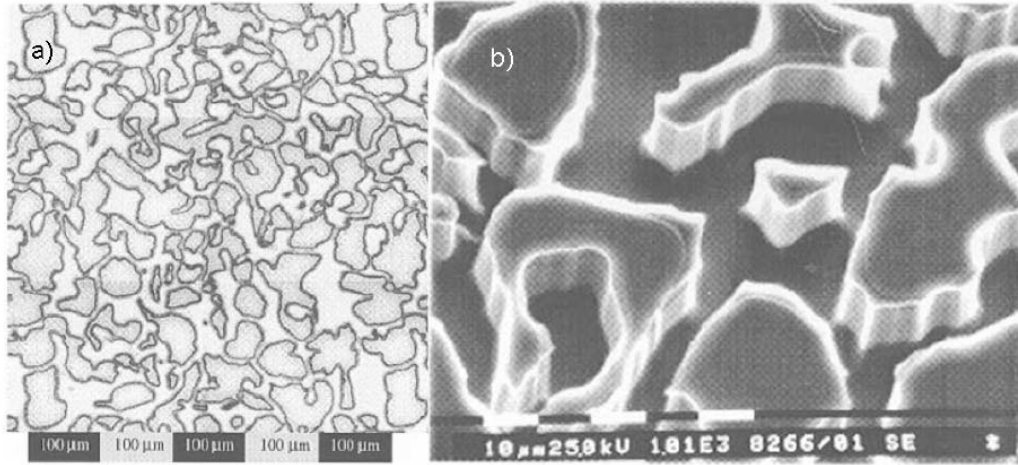


Figure 1- 21 Micro-model built with silicon [Keller, *et al.*, 1997]. (a) micro-model made by etching on silicon with thickness of 15 μm . (b) micro-model without covered glass under SEM.

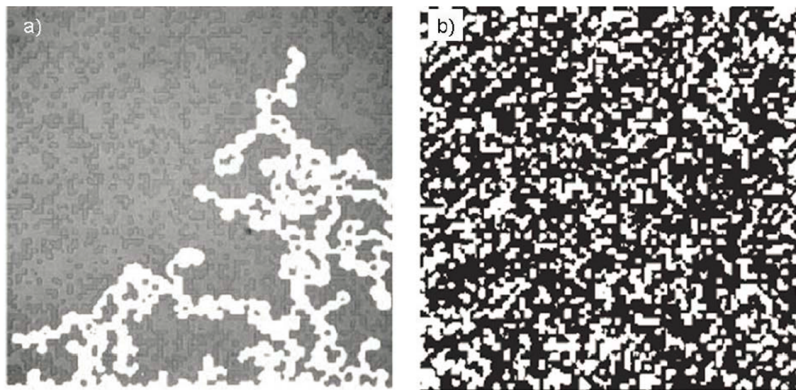


Figure 1- 22 Micro-model built with Shipley [Pyrak-Nolte, *et al.*, 2008]. (a) 2D micro-model under optical microscope. Two phases are shown. Wetting phase in gray is decane. Non-wetting phase in white is nitrogen. Solid phase in dark gray is photoresist. (b) Binary image of this micro-model.

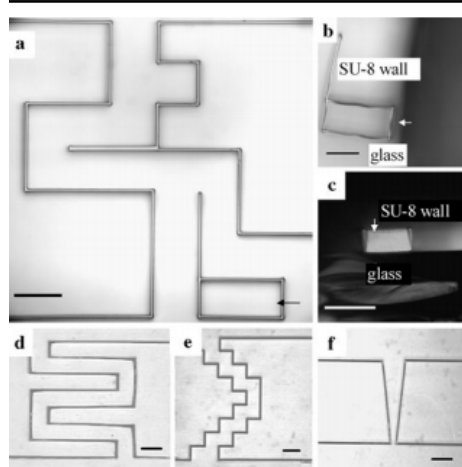


Figure 1- 23 Micro-model built with SU-8 [Liu, *et al.*, 2010]. (a) (d) (e) (f) are different patterns under optical microscope. (b) (c) are side view of the wall after cutting the cover slip.

In summary, investigations of pore scale fluid behavior have been performed on variety of micro-models. The high detection resolution and flexible pattern design make micro-models a remarkable choice to verify theories and computational simulations in porous media. Its transparency makes it possible to directly image and measure important variables such as saturation, IAV and curvatures.

1.3.2 PDMS Micro-Model

PDMS is an abbreviation for Poly-Di-Methyl-Siloxane. It belongs to a group of polymeric organosilicon compounds commonly regarded as silicones. PDMS is a silicone-based organic polymer that is most widely used because of its superior properties such as chemical inertness optical transparency, non-toxicity and non-flammability.

PDMS micro-models were widely fabricated and implemented for porous media research, biosensor development and other applications [Karadimitriou, *et al.*, 2013; McDonald and Whitesides, 2002; Duffy, *et al.*, 1998; McDonald, *et al.*, 2000; DeBusschere and Kovacs, 2001].

1.3.2.1 Rapid Prototyping

A common approach for fabricating a PDMS micro-model is called rapid prototyping. It begins with the production of a PDMS master. The master is a mold with a counter pattern to that

which will form in the PDMS. The PDMS is a mixture of two parts (liquid pre-polymer) that is poured over the master. After curing for a time, the PDMS is peeled off of the master. The PDMS has the reversed pattern of the surface of the master. A variety of methods have been used to create masters. For instance, DeBusschere and Kovacs used a machined aluminum mold [DeBusschere and Kovacs, 2001], while Duffy, et al. applied a photolithographic method to fabricate a master [Duffy, et al., 1998]. Photoresist and a mask were combined to create a selected pattern. PDMS can maintain the feature of a master with a high fidelity (~ 10 's of nm) [McDonald and Whitesides, 2002]. The master can be reused due to low surface free energy and elasticity of PDMS that maintain the pattern. A photolithographic approach for generating a master is shown in Figure 1.24 for reference.

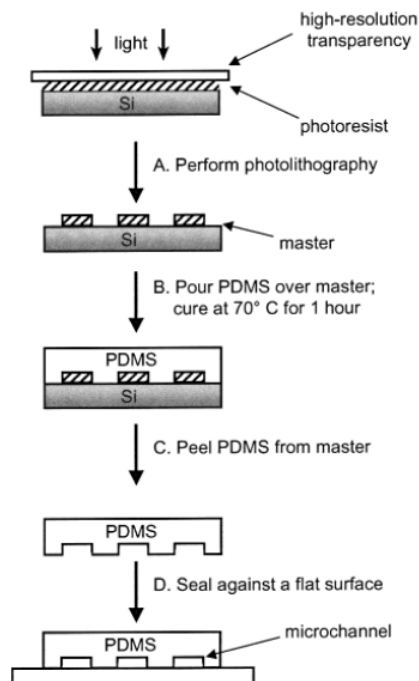


Figure 1- 24 Steps for building a PDMS micro-model via rapid prototyping. Step A: Apply photoresist and create certain pattern to make the master. Step B: Pour PDMS onto master and cure it. Step C: Peel off the PDMS from the master. Step D: Seal the micro-model onto a substrate.

1.3.2.2 Sealing

Sealing is another important step especially in microfluidic applications. An advantage of PDMS is that it can be sealed reversibly or irreversibly depending on the method. Reversible methods include simple van der Waals contact that can withstand pressures less than ~5 psi [McDonald, *et al.*, 2000], and adhesive tapes such as silicone or cellophane [McDonald, *et al.*, 2002]. However, the low-pressure limit of the tapes restricts their application.

The most widely used irreversible sealing method is to expose the PDMS and the other surface to an air plasma for 1 min [McDonald, *et al.*, 2000; Chaudhury and Whitesides, 1991]. It is believed that this operation forms silanol groups (Si-OH) on the surface of PDMS after oxidation of methyl groups [McDonald and Whitesides, 2002; Owen and Smith, 1994]. This treatment allows PDMS to be sealed with itself, silicon, glass, polystyrene silicon nitride or polyethylene.

Another irreversible method to seal PDMS was proposed by Unger *et al.* [Unger, *et al.*, 2000]. Two slabs of PDMS were prepared in different ways. Slab A is mixed with an excess of the base part and slab B is mixed with an excess of the cure part. After the reaction, the two slabs were placed in contact. With slab A having an unreacted base part and slab B having an unreacted cure part, the two slabs continue to react after sealing. This method only applies to micro-models with pure PDMS. PDMS cannot be sealed with other materials by means of this approach.

CHAPTER 2. EXPERIMENTAL METHODS

Micro-models with EWOD enable testing of the theoretical hypothesis that P_c is sensitive to changes in saturation and IAV. By applying a voltage to a micro-model with EWOD, capillary pressure can be changed by altering the interfacial curvatures, or by merging or splitting small droplets in a micro-model to alter the IAV. To obtain the relationship among capillary pressure, saturation and IAV, and furthermore to verify the constitutive equations of capillary pressure, building a micro-model with EWOD setup is the chief goal of this investigation. Development of an EWOD enabled sealed micro-model was approached in steps. The first step is to build an EWOD set-up and experiment with materials to determine the properties required to perform EWOD experiments. Selection of the right properties will yield large changes in contact angle with the application of voltage, and in turn result in visible changes in saturation. The second step is to use the selected materials to build a sealed micro-model for testing $P_c - S - IAV$ concept.

2.1 EWOD Experiments

2.1.1 Sample Preparation

Two materials were tested as a potential dielectric layer in EWOD system. The first was Polyimide (P84 Polyimide Solution in NEP) from Evonik (Batch No. 31346017) diluted with DMF (N, N-Dimethylformamide) from Macron (Batch No. 0000083032) with a volume ratio of 3:1 (Polyimide:DMF = 3:1, volume). The second material was PDMS (184 Silicone Elastomer Kit) from Dow Corning Corporation (LOT: 0008108129). PDMS was prepared by mixing 184 silicone elastomer base and 184 silicone elastomer curing agent with a mass ratio of 10:1. The material properties of Polyimide and PDMS are given in Table 2.1.

Table 2- 1 Comparison of properties of Polyimide and PDMS.

	Polyimide	PDMS
Dielectric Constant (At Low Frequency)	~3.4	~2.7
Viscosity (centipoise)	N/A	3500
Color	Yellow	No color
Static Contact Angle	~70°	~120°
Saturated Contact Angle	~30°	~40°
Chemical Properties	Very stable, partially dissolved in DMF	Very stable, not dissolved in organic solvents
Hardness	Pretty stiff	soft

The procedure for building an EWOD sample is described in steps in the following sections:
(1) Substrate preparation; (2) Metal evaporation; (3) Coating on substrate; (4) Curing.

2.1.1.1 Substrate Preparation

18 x 18 mm No.2 cover glasses with thickness of 0.17 – 0.25 mm (Cat. No. 2855-18) from Corning were used as substrates. Slides were cleaned with a Q-tip with Acetone and placed in a slide holder. The slide holder was then placed in a 140 mL beaker with Acetone or Isopropyl Alcohol with all slides immersed. Then the beaker was placed in an ultrasonic cleaner (Branson 1510) for 10 min. After two washings with Acetone and two with Isopropyl Alcohol, the slides were dried with ~100kPa Nitrogen gas.

2.1.1.2 Metal Evaporation

After drying, the slides were placed inside an evaporator to evaporate a layer of 50 nm silver to make an electrode on the slide.

2.1.1.3 Coating on Substrate

A silver-evaporated slide was placed in a chuck of a spin coater (Model P6700) from SCS. A vacuum was pulled to hold the slide in place. Two drops of Polyimide or PDMS were dropped on the slide. The slide was spun coated for 30 sec (Polyimide with 5000 RPM and PDMS with 8000 RPM). For both materials, bubbles may remain on the substrate which lowers the quality of sample. Care is taken to avoid bubbles formation as much as possible.

2.1.1.4 Curing

After spinning, the slides with Polyimide were placed on a hotplate with a temperature that increases at a rate of 5 °C per minute until 250 °C was reached. The slides were then kept at 250 °C for 1 hour. After that, the slides were cooled down with a decreasing rate of 5 °C per minute to avoid breaking the Polyimide's structure. As for the slides with PDMS, they were placed on a hotplate at 70°C for 2 hours and then cooled down to room temperature. The samples with electrodes and dielectrics (Polyimide or PDMS) were ready.

2.1.2 Single-Plate EWOD Experimental Setup

Single plate EWOD enables testing of the dielectric layer properties on the change of contact angle. The experimental setup for single-plate EWOD is shown in Figure 2.1. A slide with Polyimide or PDMS covered with a silver electrode was connected to ground. A platinum wire was inserted into a 10 μ L droplet of 1M KCl-H₂O solution and connected to an AC voltage source. A function generator from Stanford Research Systems (Model DS345 synthesized function generator) was connected to an amplifier from Trek, inc. (Model 50/750 amplifier) to create an electric field. Measurements were made for a range of voltages (V_{rms}) from 0 to 425 V at a frequency of 50 Hz. A CCD camera was used to image the side view of the droplet to determine changes in the contact angle of the droplet with applied voltage. The results are presented in Chapter 3.

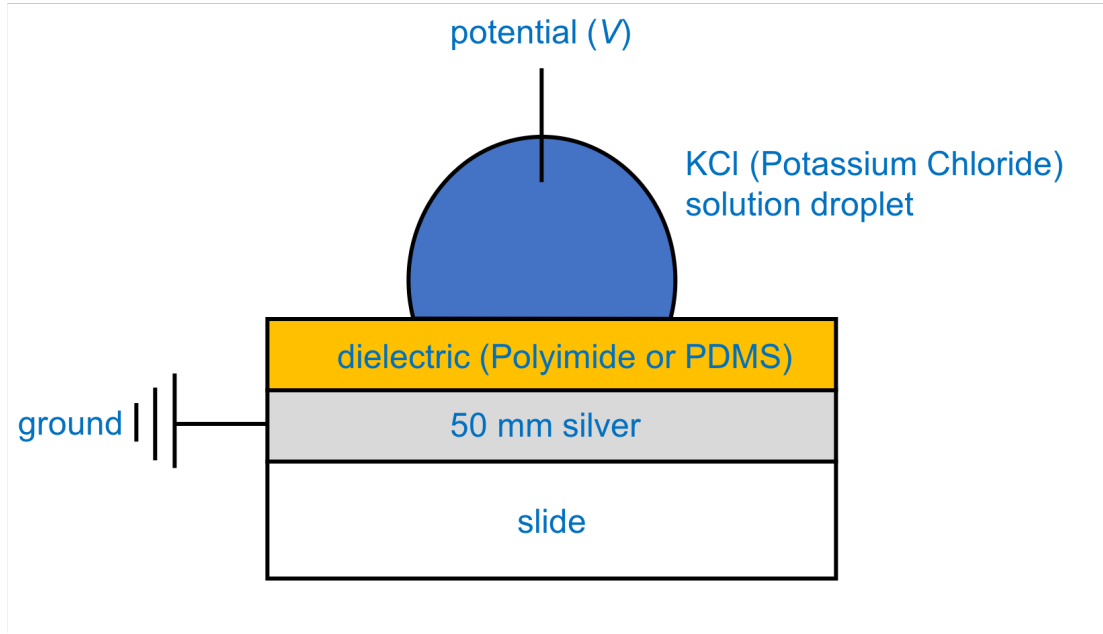


Figure 2- 1 Experimental setup for single-plate EWOD experiment. A layer of 50 nm silver was evaporated onto a slide. A layer of Polyimide or PDMS was then spun on. A droplet of 1 M KCl (Potassium Chloride) solution was placed on with a platinum wire inserted and connected to high potential. The silver was ground.

2.1.3 Double-Plate EWOD Experimental Setup

Double-plate EWOD was performed to develop the methods for fabrication of sealed micro-models with EWOD and to examine drop merging and transporting. The double-plate EWOD experiment was only performed with PDMS because Polyimide was determined to be an inferior dielectric material for EWOD. This will be shown in Chapter 3. The preparation of the double-plate experiment was similar to the single-plate approach but with some modifications. The most important difference for the double-plate EWOD experiments was the fabrication of slides with discrete electrodes which was achieved using photo resist. The steps for fabricating a double-plate EWOD device are given below.

2.1.3.1 Substrate Preparation

This step was the same as that used for single-plate EWOD substrate preparation (see section 2.1.1.1).

2.1.3.2 Spin Coating with Shipley 1805

After cleaning and drying, the slides were placed on the chuck of a spin coater one at a time. Two drops of Shipley 1805 were placed on to the slide. The slide was then spun with a spin rate of 3000 rpm.

2.1.3.3 Soft Baking

The slides were then place on a hotplate at 90 °C and soft-baked for 30 min.

2.1.3.4 Exposure

Next, the slides were placed under a 400 nm UV LED array for 2 min with a special mask. The mask is shown in Figure 2.2a. Shipley 1805 is a positive photoresist. After development, the area exposed to UV light is removed.

2.1.3.5 Development, Cleaning and Drying

After exposure, the slides were then placed into a slide holder and placed into a solution of 351 developer from Microposit (Batch code A016C7O019) diluted with water using a volume ratio of 1:3.5 for 30 sec. Residues of developer were cleaned by placing the holder into diluted water for 60 sec twice. The slides were then dried with 100kPa Nitrogen gas.

2.1.3.6 Evaporation

This step was the same compared to single-plate EWOD substrate preparation (see section 2.1.1.2).

2.1.3.7 Shipley 1805 Removal

Shipley 1805 is dissolved in Acetone. The slides were washed in Acetone and then in Alcohol, two times for 5 min. The resulting pattern is shown in Figure 2.2d.

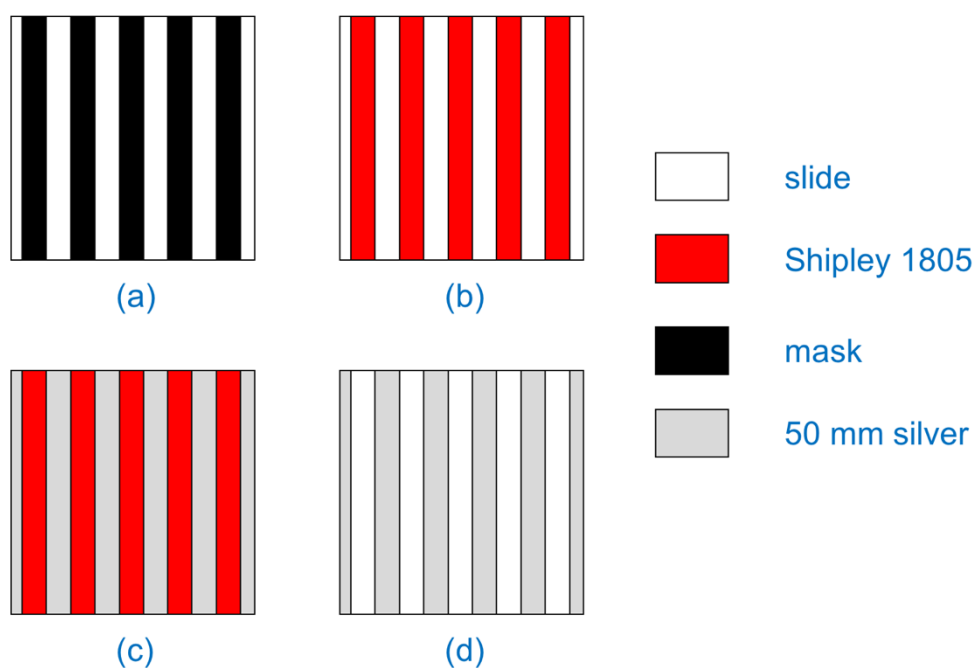


Figure 2- 2 The pattern of required mask in this experiment (a), the remained photoresist pattern after development (b), the pattern after evaporation of silver (c) and the pattern of the electrodes after removing remained photoresist(d).

2.1.3.8 Device

One slide with discrete electrodes and a second slide with one electrode were used to compose the two-plate open-sided EWOD device (Figure 2.3). The other slide with discrete electrodes was connected to high voltage controlled by independent switches that were placed in parallel to the first slide with the dielectric & electrode side face to face. After dropping one or two 10 μL droplets of 1M KCl-H₂O solution, the top plate was lowered into contact with the droplet(s). Voltage was applied on different electrodes via switches to enable the transport of droplet(s).

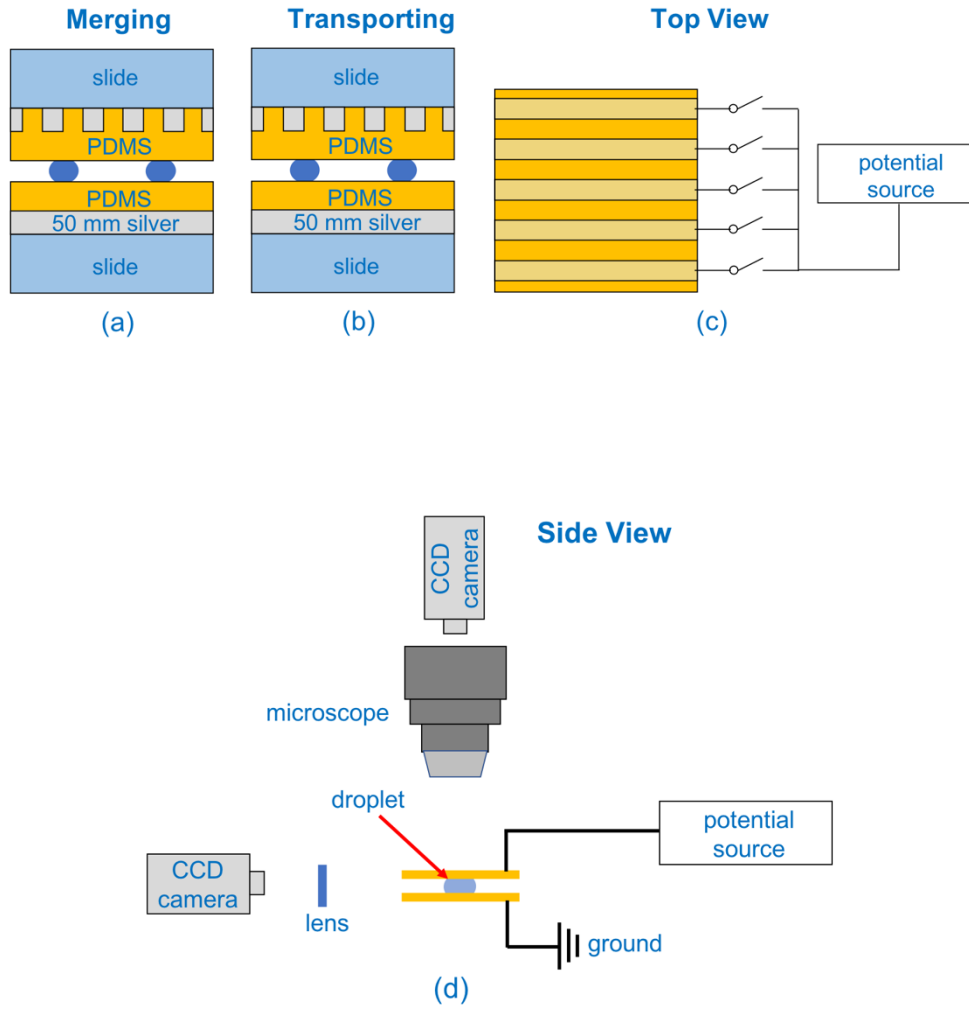


Figure 2- 3 Experimental setup of double-plate experiment. (a) is an outlook of the merging experiment. (b) shows transporting experiment. (c) displays the discrete electrodes. And (d) exhibits the general setup.

2.2 Fabrication of Micro-Model with EWOD

In section 1.3.2, it was mentioned that rapid prototyping is the easiest way to build a PDMS micro-model. In this research, a modified prototyping method was used that included a method for insertion of electronics. The fabrication protocol for sealed micro-models with EWOD is described in the following sections.

2.2.1 Mold Building

The first step in prototyping is to build a mold to create the channel and fluid reservoirs. Formlabs 3D printer (Form 2) was used to produce a master. Before 3D printing, the mold was designed with Autodesk Inventor software. The design is shown in Figure 2.4. The channel is wedged shaped with an outlet of 0.5 mm and an inlet of 2 mm. The distance between the inlet and the outlet is 4 mm. The two sides are connected to square fluid reservoirs with dimensions 5 mm x 5 mm. Depths of 0.3 mm, 0.6 mm and 0.9 mm were designed for experiments to examine the effect of aperture on fluid behaviors. During 3D printing, a resolution of 0.025 mm was selected to achieve a smoother surface. Figure 2.5 has additional views of the printed mold.

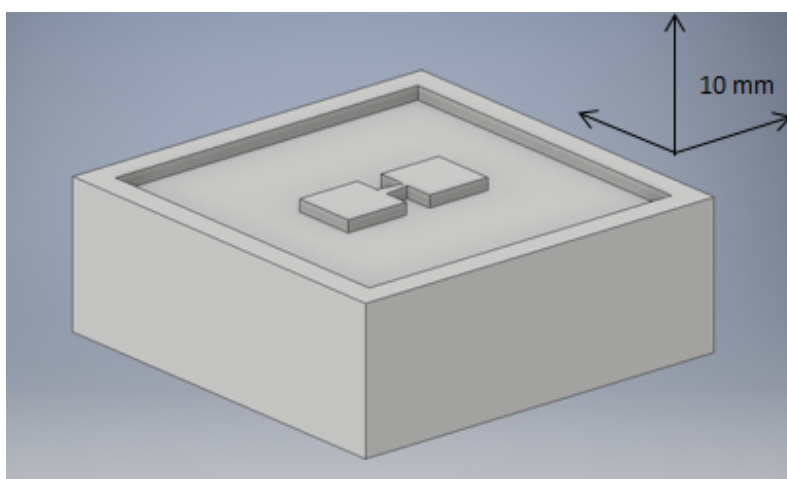


Figure 2- 4 The design of mold for fabricating PDMS micro-model in Inventor. The outside wall is 1 mm and the channel pattern 0.9 mm.

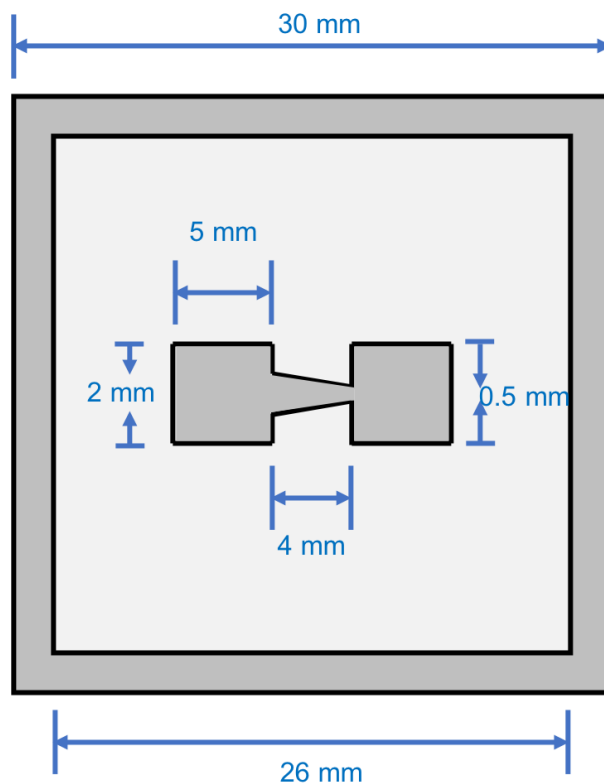


Figure 2- 5 A top view with scales and a real image of the mold made by 3D printing with resolution of 0.025 μm .

2.2.2 Preparation of the Ground Electrode

The inclusion of electronics into a micro-model complicates the design for ports. The fluids should never touch the electrodes so the system will not short out. The system should be stable and easy to seal. Here, an aluminum plate instead of a glass slide was used as the ground electrode

because of several advantages, e.g. it is conductive and easy to drill holes for connecting ports. Aluminum plates from McMaster Carr (Easy-to-Weld Corrosion-Resistant 5052 Aluminum) were cut into 60 x 20 mm pieces. Two 10 mm x 5 mm rectangular pieces were removed from each Aluminum piece using a band saw. This enabled the electrode in the channel area to be retained while in the removed area, PDMS was used to isolate the ports. After machining, the Aluminum pieces were cleaned in acetone and in alcohols two times each for 5 min.

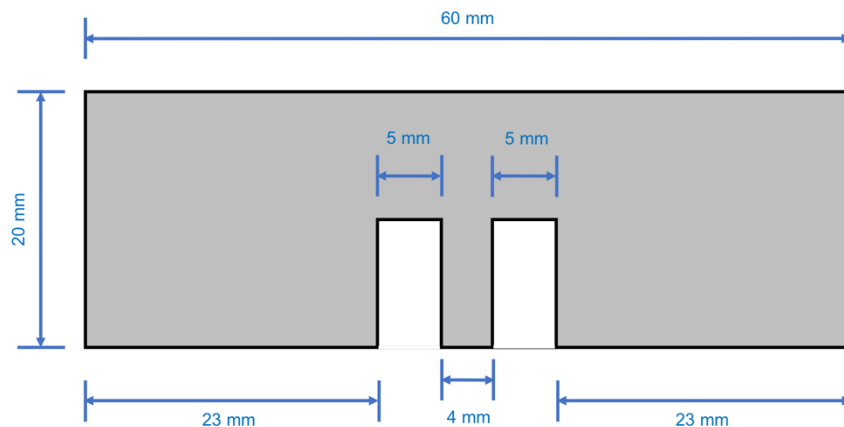


Figure 2- 6 A top view of Aluminum plate after cutting off two 10 x 5 mm pieces separated by 4 mm.

2.2.3 Preparation of Channel

PDMS was prepared by mixing the base part (Sylgard 184 silicone elastomer base) and the cure part (Sylgard 184 silicone elastomer curing agent) with a mass ratio of 10:1. The mixture was placed in a vacuum environment for 30 min to degas the PDMS. After 4 h, the mixture was slowly poured onto a mold. Care was taken to ensure the sample was level to form a uniform thickness of PDMS. An Aluminum piece was placed onto the PDMS with the open area aligned above the reservoirs on the mold. Two small cylinders with outer diameters of 2.8 mm were placed in the center of each reservoir on the mold through the open area of the Aluminum piece. Care was taken to avoid air bubbles in the PDMS layer as much as possible. The entire part was left at room temperature for 24 h to allow the PDMS mixture to continue to react. After curing for 24 h, the Aluminum piece associated with the channel was peeled off from the mold. Great care was taken to avoid breaking or tearing the channel.

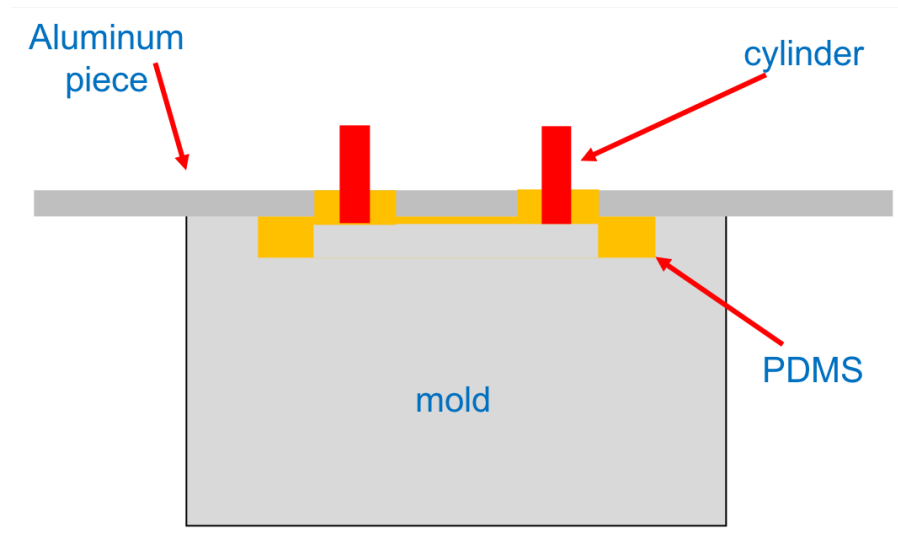


Figure 2- 7 Cast PDMS onto the mold and then cover it with Aluminum piece. The cylinders (red) were placed on mold to create ports.



Figure 2- 8 This shows the pattern after peeling off the channel with Aluminum piece from the mold.

2.2.4 Preparation of Ports Connection

Ports were designed and 3D printed to create ports that were isolated from the electronics and that easy to connect external equipment. As shown in Figure 2.9, this port component enabled separation of the fluids and the electronics. This piece was then attached to the channel piece using PDMS with 2.8 mm cylinders inserted in layer. Side and top views are shown in Figure 2.10. The channel connected to external fluids using tubing that is tightly inserted into the holes in the bottom piece.

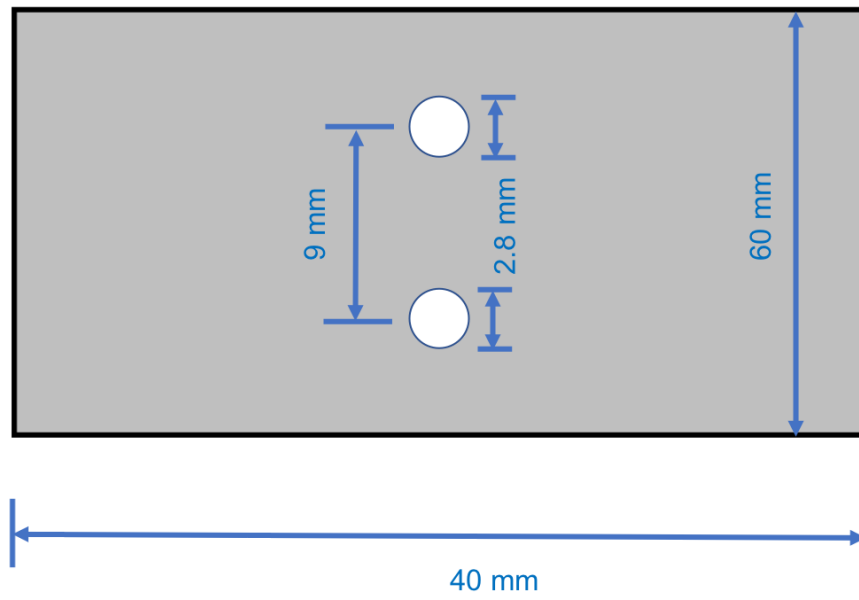


Figure 2- 9 The scales of the bottom piece.

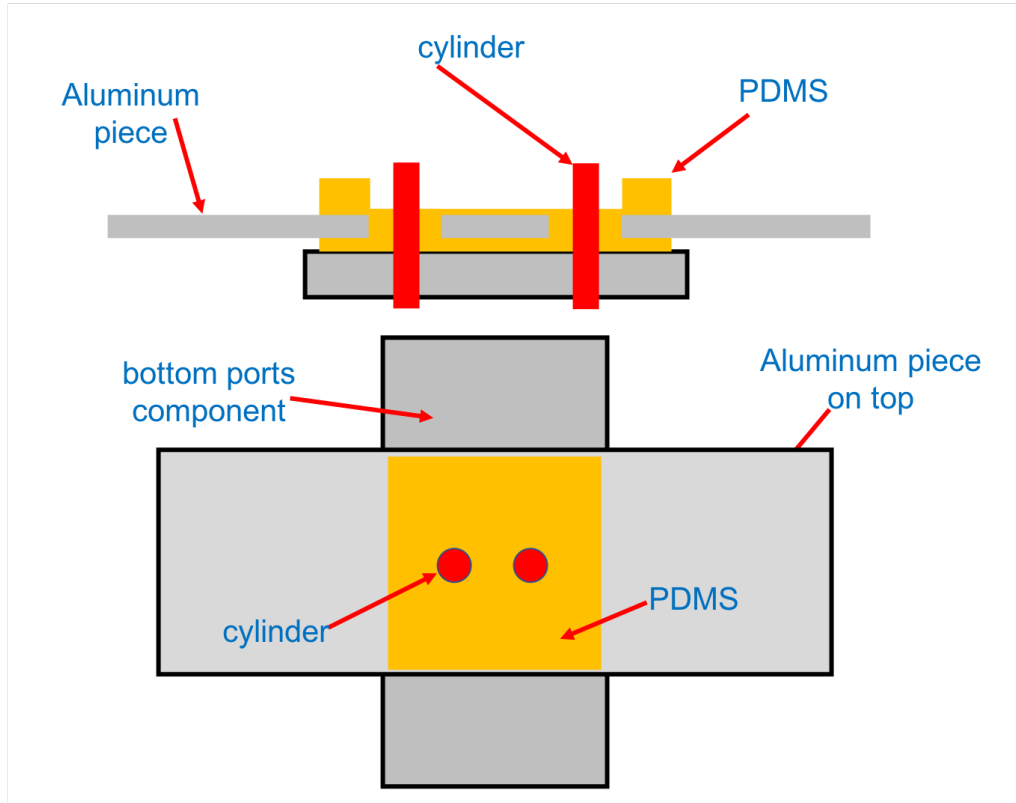


Figure 2- 10 Attach the bottom piece to the channel piece with PDMS. Side view and top view are given.

2.2.5 Covered Slide on Top

Before sealing the micro-model, a covered slide was prepared. Unlike the open EWOD experiment, for the sealed EWOD, an ITO (Indium Tin Oxide) slide from Sigma Aldrich (Product No. 703192-10PAK) was used instead of a silver-evaporated slide. ITO was selected because of its superior properties such as transparency and good conductivity. The ITO slide provides a better view of the channel compared to silver coat.

Before sealing, electrodes were created on the ITO cover glass with PDMS. When discrete electrodes are needed on the slide, ITO is locally removed cursing a diamond scribe to created isolated electrodes.

2.2.6 Preparation of Top Slide and Sealing

As a final step, sealing is one of the most important steps in the fabrication of a micro-model. In section 1.3.2, it was mentioned that plasma is the most widely used method to seal a

PDMS micro-model. However, in this approach, plasma is not applicable because during plasma application, no electronic components should be present. Another method mentioned in section 1.3.2 proposed that, by changing the ratio of the two parts that make PDMS (with one side having an over-ratio of base part and the other side having an over-ratio of cure part), the two parts can continue to react and seal after placing them in contact. This method was not used in our fabrication because a very thin layer of PDMS spun on the ITO slide is required, thus it's very hard to get complete contact between the two parts.

For this work, I developed a new method to seal a PDMS micro-model with inspiration from the above method. The method is described below:

First, the base part and cure part of PDMS were mixed with the proper mass ratio (10:1). After degassing for 30 min, PDMS was spun on ITO slide at a spin rate of 3000 rpm. The ITO slide coated with PDMS was then laid flat at room temperature for 6 – 10 hours. By doing this, the mixture partially reacted. The PDMS on the ITO slide had already formed the flat surface but was still sticky enough to react. After that, the PDMS coated ITO slide was turned over and placed on the channel piece. By applying a small force by pressing with a finger, the two surfaces were brought into perfect contact. The combined pieces were then placed flat on a table at room temperature for another 24 h. After doing this, the PDMS micro-model was sealed. In these steps, the good waited time after spinning (6 – 10 hours) was tested many times. During all the steps, high temperature was not applied because it would result in imperfect sealing. With this approach, I was able to fabricate sealed PDMS micro-model with EWOD setup with a yield rate of 60%.

This step was shown in Figure 2.11.

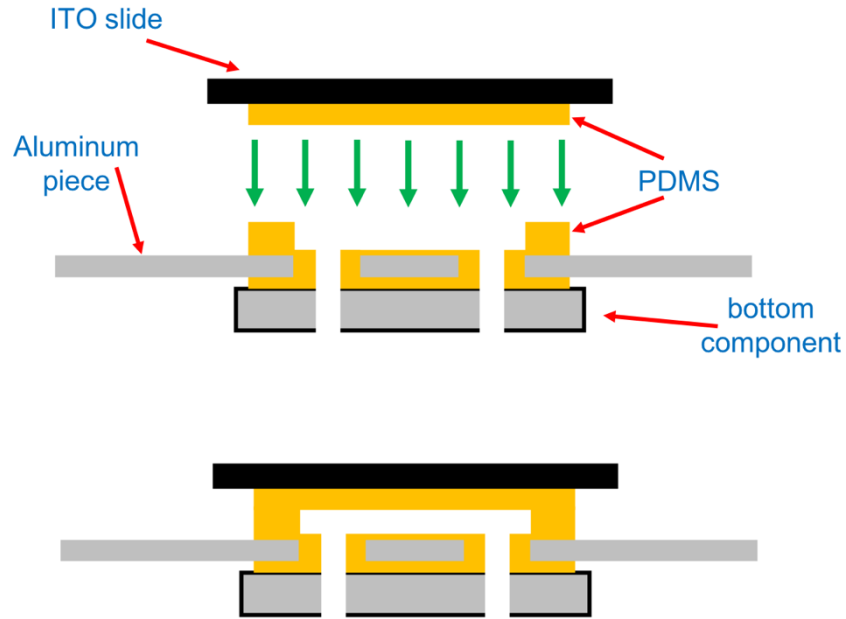


Figure 2- 11 Preparation of the top covered slide. By spinning PDMS on ITO slide and waiting for 6 – 10 h, The micro-model is sealed by attaching them together.

2.2.7 Other Channel Patterns

In addition to the wedged-shape channel, other patterns were used that included a step pattern and a multi-cylinder pattern (Figure 2.12). For the step pattern, it has five 0.8 mm x 0.2 mm steps. For the multi-cylinder pattern, it has 6 x 6 cylinders with diameters of 2 mm.

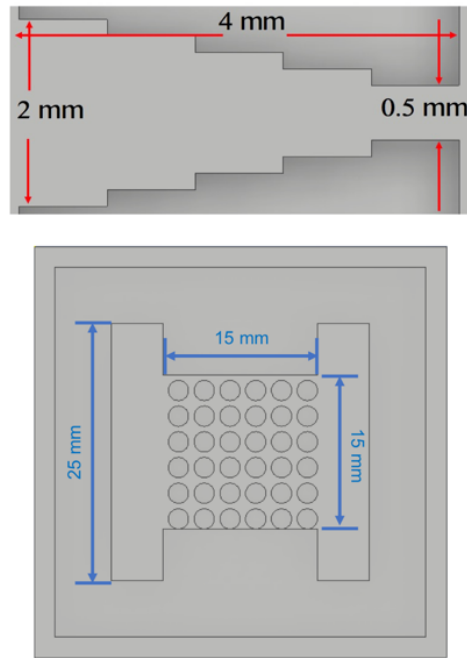


Figure 2- 12 Other patterns of micro-model used in this thesis. The upper is a 5-step channel and the lower is a multi-cylinder channel.

2.3 Micro-Model Experimental Approach

2.3.1 Experimental Setup

The experimental setup for measuring P^c , and S in a micro-model with and without applied voltage is shown in Figure 2.13. A microscope (Nikon Eclipse LV150) with a CCD camera (QIMAGING Retiga-2000DC) was used to acquire images of the channel during the experiment with a frame rate of 1 fps. Two fluid phases, 0.01 M Potassium Chloride (KCl) solution that contained dissolved fluorescent dye Alexa-fluor 488, and air were introduced into the micro-model from two separated reservoirs into the wedge-shaped channel. The pressure of the water was controlled by adjusting the height of the solution level in a syringe attached to a stage. The head was controlled with a micrometer that was used to raise or lower the stage. The water pressure was measured with a pressure transducer from OmegaDyne (0 – 2 psi). In an open system, the air phase was open to the atmosphere and thus not recorded. The water pressure transducer measured the pressure relative to atmospheric pressure. In a close system, the pressure of the air was controlled with a syringe connected to a pump and was also monitored with a pressure transducer from

OmegaDyne (0 – 1 psi). Both transducers were connected to digitizers from National Instruments (NI USB-4065) and recorded with sample rate of 1 sec⁻¹. Tubing from Smiths Medical was used to connect all parts described above. One wire from the voltage source was connected to the electrode area on the top glass. Another wire was connected to the bottom Aluminum piece to act as the ground.

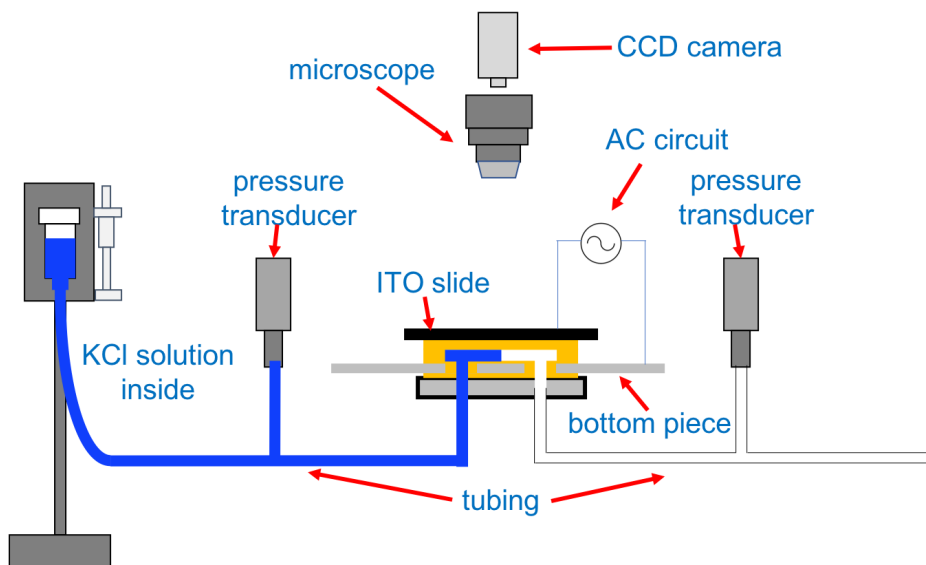


Figure 2- 13 Sketch of experimental set-up for the effect of EWOD in micro-model. The fluid pressure is controlled by micrometer and the air pressure is open to atmosphere. One or two pressure transducer(s) connected to Ni voltage meter(s) is (are) used to record pressure(s). Microscope with camera on top is used for image acquisition of the channel. Voltage source is used to apply external voltage on the micro-model.

CHAPTER 3. EXPERIMENTAL RESULTS OF ELECTRO-WETTING ON DIELECTRIC (EWOD)

3.1 Single-Plate EWOD

As mentioned in section 1.2, with the application of a potential difference between a wire inserted in a droplet placed on a dielectric coated electrode, the shape of the droplet varies. The cosine of the contact angle changes linearly with the square of the applied potential difference at low voltage [Verheijen and Prins, 1999] and tends to a constant value as the potential increases to infinity. The goals of performing single-plate EWOD experiments were:

1. To determine the material to use as the dielectric to yield the greatest changes in contact angle with/without application of EWOD.
2. To determine the fluid solutions and AC frequency to using in the experiments.

A series of experiments were performed on single-plate EWOD setup to obtain this information.

3.1.1 Material

In the single-plate experiment, two materials, Polyimide and PDMS were tested with single-plate EWOD. The sample preparation and single-plate EWOD setup are described in sections 2.1.1 and 2.1.2, respectively. In this experiment, an AC frequency of 50 Hz and 1M KCl solution was used. The change in $\cos \theta$ as a function of the square of the applied voltage is given in Figure 3.1.

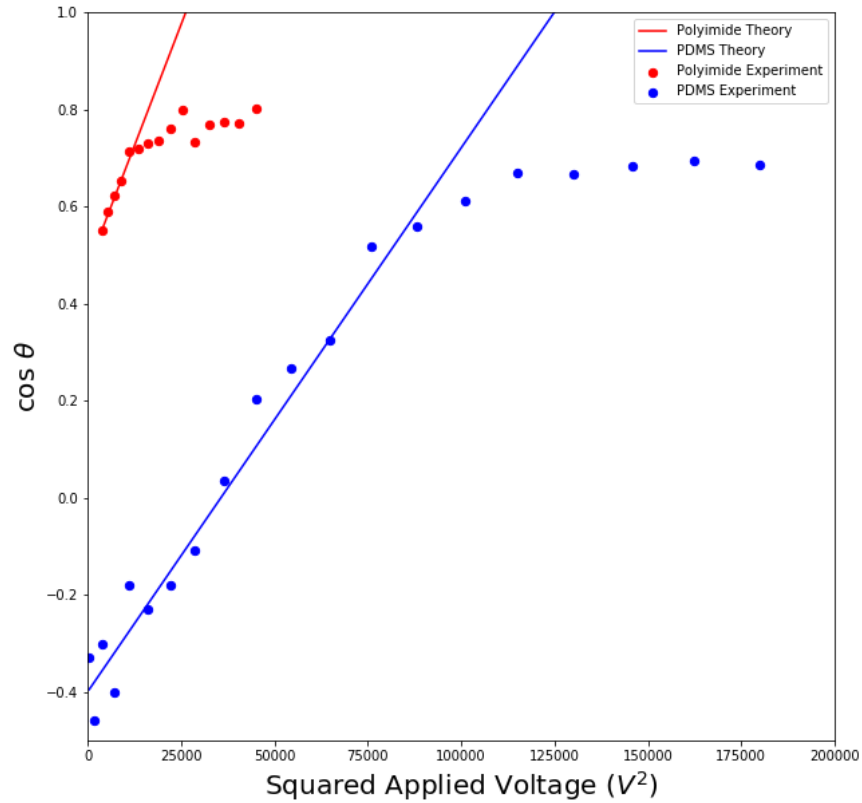


Figure 3- 1 Relationship of $\cos \theta$ vs. V^2 of Polyimide and PDMS. Originally Polyimide is a wetting material (θ is less than 90°) and PDMS is a non-wetting material (θ is great than 90°). Both two materials show a linear relationship between $\cos \theta$ and V^2 at low voltages and become saturated at high voltages.

By applying a voltage, whether through a liquid droplet on Polyimide or PDMS, the contact angle was observed to change. The contact angle decreased as the voltage increased. Both Polyimide and PDMS samples exhibited linearity in $\cos \theta$ vs V^2 at relatively low voltage. When the voltage was increased, $\cos \theta$ saturated.

For a droplet placed on Polyimide, the initial contact angle was less than 90° , indicating that Polyimide is aqueously wetting. In section 1.2.1, it was mentioned that the measured contact angle in an experiment is highly dependent on the roughness of the surface and the manner of placing the droplet. In this experiment, the contact angle without voltage was approximately 60° . By applying a voltage, the contact angle decreased to as low as 35° .

For the PDMS substrate, the initial contact angle was greater than 90° , indicating that PDMS is aqueously non-wetting. The contact angle was $\sim 120^\circ$ before voltage was applied. The saturated contact angle was $\sim 45^\circ$ at high voltage.

Based on the linearity of $\cos \theta$ vs V^2 , the thicknesses of the Polyimide and the PDMS layers were calculated via Eq. 1.28 and are shown in Table 3.1:

Table 3- 1 Experimental data of Polyimide and PDMS.

	Polyimide	PDMS
Dielectric Constant (At Low Frequency)	~ 3.4	~ 2.7
γ_{lv} ($\text{mN}\cdot\text{m}^{-1}$)	72	
ϵ_0 ($\text{C}^2\text{N}^{-1}\text{m}^{-2}$)	$8.85\text{e-}12$	
Slope of the linearity ($\text{C}^2\text{N}^{-2}\text{m}^{-2}$)	$8.04\text{e-}6$	$1.121\text{e-}5$
Thickness (μm)	26.12	14.8

From the experimental results, PDMS exhibited a wider range of contact angles than that observed for the Polyimide substrate for the same range of voltages. For this research, PDMS was the better choice because the difference between a wetting versus a non-wetting fluid could be explored for the same channel geometry.

Also, as mentioned in section 1.3, PDMS is a widely used material for fabricating micro-models.

For these reasons, all experimental results from the open and sealed micro-model were obtained from micro-models or chips that contained PDMS as the dielectric layer.

3.1.2 Frequency

As shown in section 1.2.4, when the AC frequency is far below the critical frequency, the droplet can be treated as a perfect conductor. Different frequencies were tested with 1M KCl solution at $V_{\text{RMS}} = 212$ volts ($V_{\text{max}} = 300$ volts) to explore the frequency limit of the setup. The results are shown in Figure 3.2.

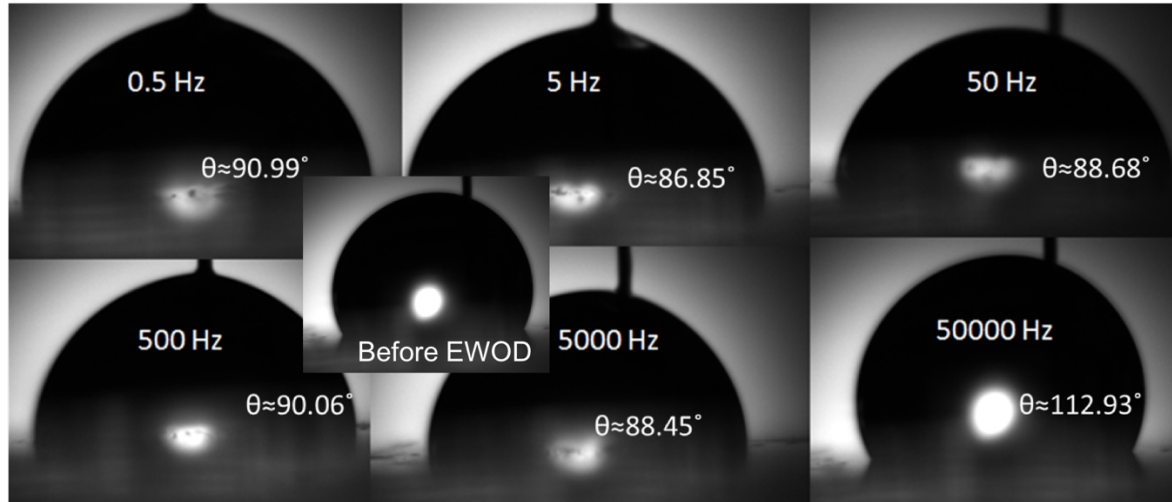


Figure 3- 2 Influence of frequency. The droplets were 1M KCl solution. V_{RMS} of 212 volts ($V_{max} = 300$ volts) were applied through a platinum wire and a ground plate. The frequencies vary from 0.5 Hz to 50, 000 Hz. Frequencies lower than 5, 000 Hz exhibits similar results, EWOD was in effect. With frequency of 50,000 Hz, the droplet didn't change.

The experimental results show that when the frequency is lower than 5,000 Hz, with EWOD the frequency does not significantly affect the contact angle. At high frequency, the frequency is not small enough compared to the critical frequency (see section 1.2.4). The droplet does not behavior like a perfect conductor, and EWOD effect is no longer apparent. The shape of droplet is similar to the no applied voltage condition.

3.1.3 Molarity

Molarity affects EWOD because molarity of a fluid affects the surface tension (or more accurately, the interfacial tension between the droplet and atmosphere) and conductivity. The first step was to test the surface tension of the KCl solution for different molarities with an interfacial tensiometer (Du Nouy ring) from Central Scientific Co. (Cat No. 70545). The results are given in Table 3.2:

Table 3- 2 Surface tensions of KCl solution measured with different molarities.

Molarity (M)	Measured Surface Tension @ 24.3 °C (dyn per cm)	Error (dyn per cm)
1	74.34	0.0744
0.5	72.52	0.0456
0.1	73.28	0.0536
0.01	71.88	0.1216
Distilled	69.63	0.1216

From this table, generally, KCl solution has a larger surface tension compared to distilled water. The surface tension decreased with decreasing molarity.

Single-plate EWOD experiments were performed on liquid droplets with different molarities at AC frequency of 50 Hz. The results are shown in Figure 3.3.

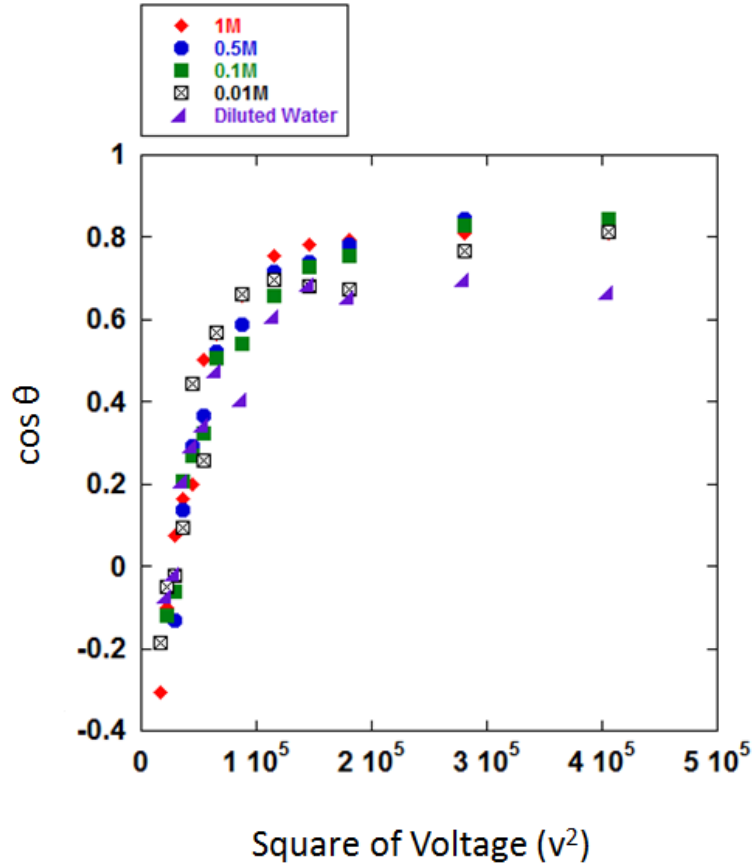


Figure 3- 3 Molarities of 1M, 0.5M, 0.1M, 0.01M of KCl solution and diluted water in EWOD experiments.

$\cos \theta$ for KCl solutions with different molarities (1M to 0.01M) do not show a significant difference when $V^2 < 10^5$. When V^2 exceeded this value, in which the liquid droplet contact angle saturated, the saturation curvatures are differed. Generally, a lower concentration yields a larger saturation contact angle.

3.1.4 Conclusions from Single-Plate EWOD

The single-plate EWOD experiments determined:

PDMS is a good dielectric material for use in fabrication of micro-models because it exhibited a significant change in contact angle ($\sim 120^\circ$ to 50°) with applied voltage enabling examination of immiscible fluid displacement in the non-wetting and wetting regimes, respectively.

An AC frequency of 50 Hz was selected because 50 Hz was easily obtainable and sufficient to produce changes in contact angle.

Molarity of 1M KCl solution was used as the liquid phase because it exhibited the widest change in contact angle with applied voltage.

These material properties and experimental parameters were used in the following double-plate EWOD and sealed micro-model with EWOD experiments.

3.2 Double-Plate EWOD

The double-plate EWOD experiments were performed on PDMS coated glass slides with evaporated electrodes. In the experiments, the slide with ground electrode was placed flatly with the PDMS layer facing up. Another slide with discrete electrodes was initially placed right above it. Droplet(s) of 1M KCl solution was (were) placed on the right side of the slide and then the top slide was lowered and connected to the droplet(s). The final aperture between two slides was ~ 1 mm. Transporting and merging were observed by controlling which electrode were off or on (Figure 3.4 & 3.5).

3.2.1 Transporting

Transporting a single droplet was performed by placing the droplet at the edge of an electrode (Figure 3.4). Before applying a voltage, the droplet spanned two electrodes. All contact angles were $\sim 120^\circ$ prior to applying the voltage difference. The right electrode was then turned on and the droplet moved toward the right. With the voltage still on, the contact angle changed to $\sim 45^\circ$. By turning off the voltage on the right electrode, the contact angles released to $\sim 100^\circ$. The droplet was transported ~ 1.3 mm.

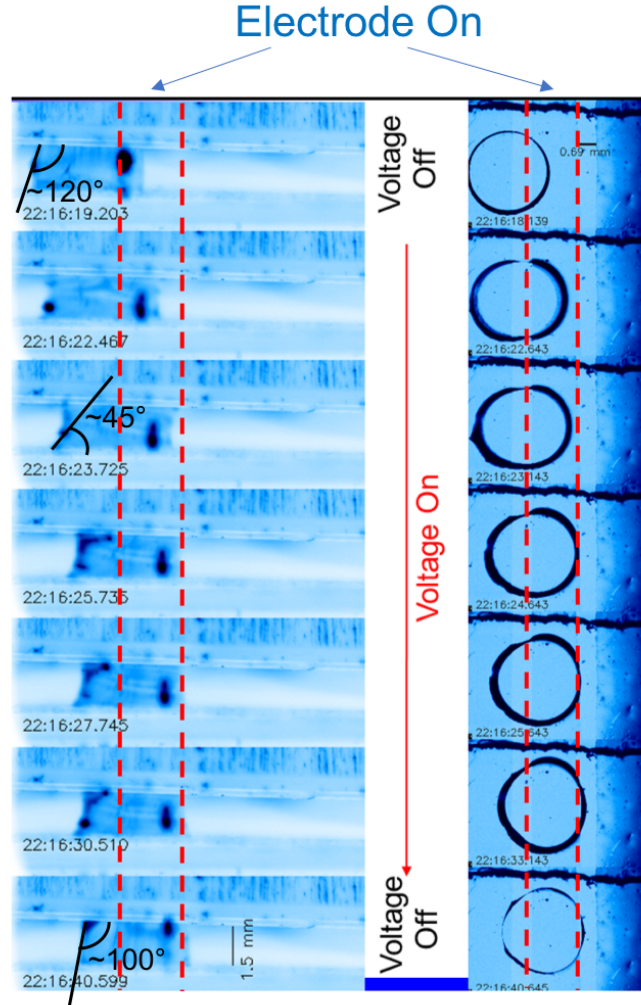


Figure 3- 4 Side and top view of transporting droplet. After applying a voltage of $V_{\text{RMS}} = 424$ volts ($V_{\text{max}} = 600$ volts) on the right electrode, the droplet moved toward right for a distance of around 1.3 mm. The electrode between dashed red lines was on.

3.2.2 Merging

Merging of two droplets was performed by placing two droplets across the two edges of the same electrode (Figure 3.5). Before applying a voltage, the two droplets spanned the two boundaries of an electrode. The original contact angles were $\sim 120^\circ$. With a time < 0.5 s after applying a voltage of 424 V, the two droplets merged together to form a larger droplet. With the voltage still on, the contact angles were $\sim 60^\circ$. By turning off the voltage, the contact angles reverted to $\sim 110^\circ$.

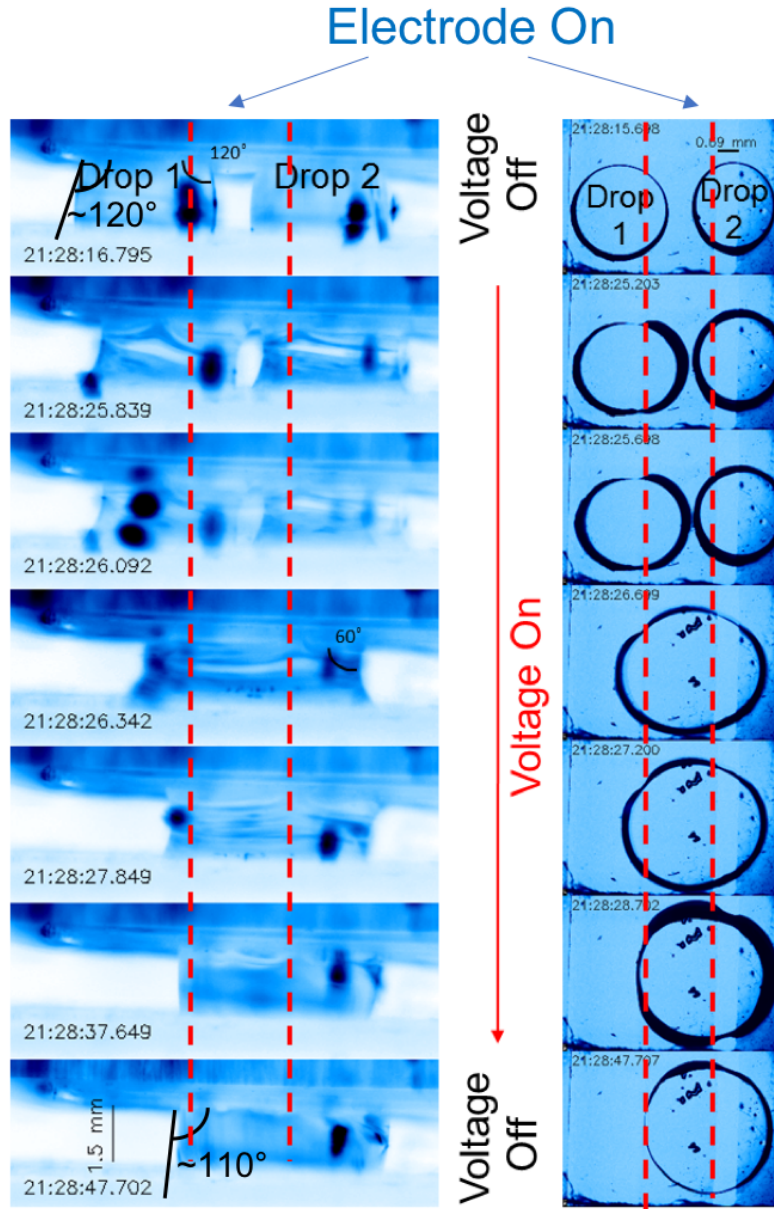


Figure 3- 5 Side and top view of merging experiment. Two droplets across two sides of one electrode merged to a bigger droplet by applying a voltage of $V_{\text{RMS}} = 424$ volts ($V_{\text{max}} = 600$ volts). The electrode between dashed red lines was on.

To calculate the pressure difference between before and after applying voltage, Eq. 1.50 is used instead of Eq. 1.51 because it was not known whether the EWOD condition was saturated or not. The calculated pressure difference was ~ 100 Pa.

3.2.3 Conclusion

In an isolated double-plate EWOD system with an aperture on the scale of a mm, by application of voltage, a pressure difference of ~ 100 Pa across a droplet was created. This pressure difference was sufficient to translate the liquid phase. It can be expected that in a continuous sealed system (micro-model), the fluid saturation can be changed via EWOD.

3.3 Conclusion for Double-Plate EWOD Experiments

In previous research, transporting, merging, and splitting of droplet(s) were performed successfully using other dielectric materials [Cho, *et al.*, 2003]. Here, in the double-plate EWOD experiments, it was proven that transporting and merging can be achieved with double-plate EWOD setup that uses PDMS as the dielectric material. These results show that manipulation of saturation in sealed PDMS micro-model with EWOD should be achievable and is demonstrated by the results discussed in the next chapter.

CHAPTER 4. EXPERIMENTAL RESULTS FOR A SEALED MICRO-MODEL WITH EWOD SETUP

The fabrication of sealed PDMS micro-models with EWOD was described in section 2.2. In chapter 3, it was demonstrated that, with the application of EWOD on one end of a liquid, the contact angle at that side decreased, resulting in a decrease of pressure, which translated a drop toward the electrode side.

Here, EWOD was applied to a resting interface at equilibrium in a micro-model channel to examine the effect of internal manipulation of contact angle on fluid pressure, IAV and fluid saturation.

A range of experiments were performed on micro-models with different channel patterns to determine the effect of EWOD on continuous fluid phase behavior for open pressure conditions. The saturation – pressure relationship was measured with/without EWOD to compare the imbibition and drainage behavior for different contact angles.

4.1 Effect of EWOD in Open System

As described in section 2.3, an open pressure system consists of an applied head at the inlet with the outlet open to the atmospheric pressure. The application of EWOD under these conditions was used to examine the effect of changes in contact angle on air-fluid interface, capillary pressure and saturation.

As shown in section 2.3.1, the fluid pressure was controlled by an adjustable head that was open to the atmosphere. The air phase was also open to the atmosphere. Imbibition and drainage experiments were performed under these open system conditions. Saturation and capillary pressure were measured with and without the application of 500 V to investigate the effect of EWOD for different initial saturations.

In this set of experiments, the interface initially equilibrated at 0.25, 0.4, 0.4, 0.55 of fluid saturation for pressures 52, 64, 72, 84 Pa, respectively. The system was maintained for 5 – 10 min prior to the application of voltage to ensure that equilibrium was reached.

In Figure 4.1, time = 0 represents when the voltage was applied. Time < 0 is during the equilibration period. The voltage was turned off 30 min later. During the 30 min, the pressures

remained constant (Figure 4.2). Fluid saturation (Figure 4.1) were obtained from analysis of images taken during the experiment (see section 2.3 for details).

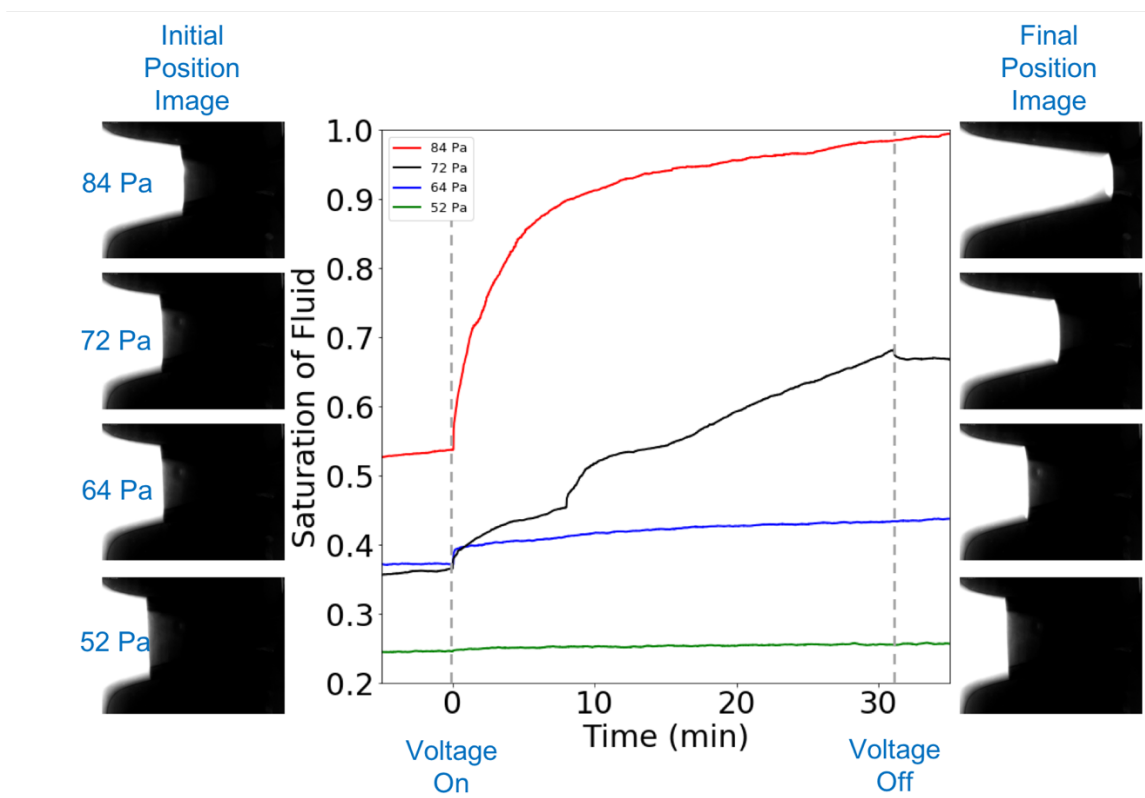


Figure 4- 1 Change of saturations after applying EWOD for different initial conditions. The green and blue didn't change much with EWOD. The black, though started at same saturation with blue, moved forward to the outlet dramatically. The red, initially at saturation of 0.55, moved almost out of channel after the voltage.

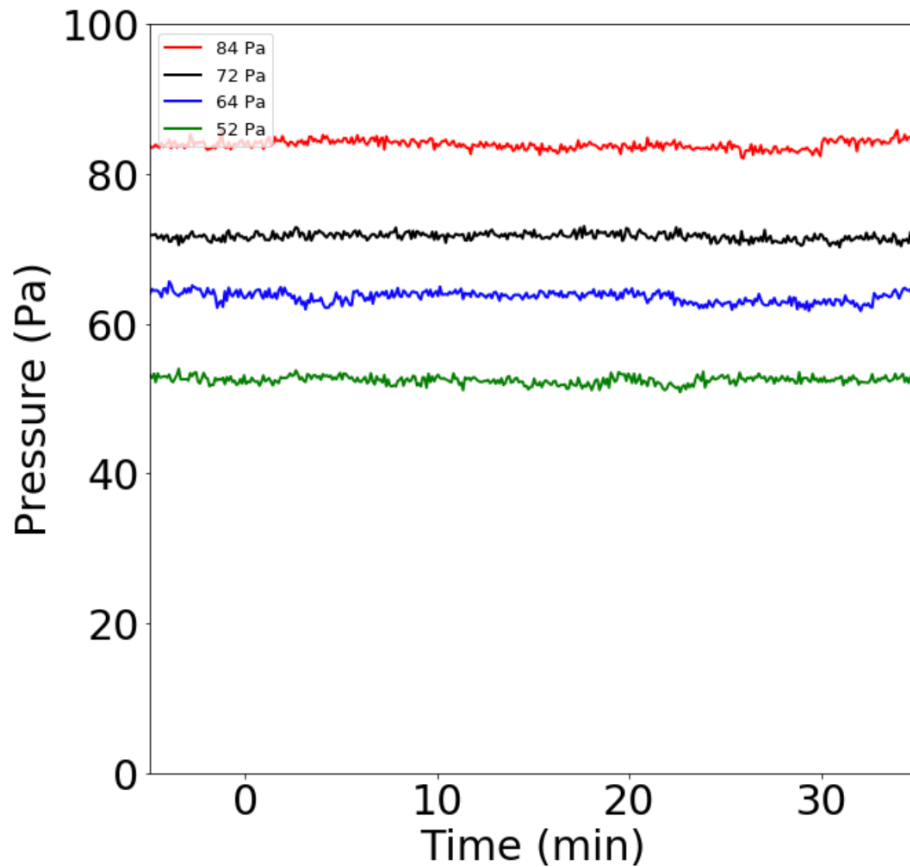


Figure 4- 2 Pressure changes for each experiment showing in Figure 4-1

In the following, pressure means the pressure difference between the liquid phase and air phase. In Figure 4.1, for a pressure = 52 Pa (green line), before the application of EWOD, the interface was near the inlet (saturation of fluid = 0.25). With the application of EWOD, the interface didn't not change significantly. For a pressure = 64 Pa and an initial saturation of fluid at 0.38 (blue line), the application of the voltage caused the interface to invade quickly into the channel with a small amount and then stopped with very little change in saturation over the remaining period. For the experiment (black line) at 72 Pa with a starting saturation of 0.37, by applying the EWOD, the interface moved a significant amount. The interface didn't reach an equilibrium state within 30 min. By turning off the voltage, the interface relaxed immediately. At pressure of 84 Pa and saturation of 0.52 (red line), the interface moved a great amount. As the interface closed to the outlet, the moving speed decreased.

The different behaviors after application of EWOD is explained by the receding-advancing contact angles. For a certain interface (in this experiment it was KCl solution – PDMS), it is able to equilibrium at different contact angles. Among those contact angles, the smallest and largest are called receding and advancing contact angles, respectively (See Figure 4.3a). In this case, if the goal is to displace air by KCl solution, the pressure of solution needs to be increased. With slow increment of pressure, the interface won't start to move until the contact angle reaches advancing. Once it reaches advancing, the interface will move at advancing contact angle (Figure 4.3b). Similarly, when it is required to displace KCl solution by air, by slowly decreasing the pressure of KCl solution, the contact angle will first reach receding contact angle remaining unmoved and start to move at receding contact angle (Figure 4.3c).

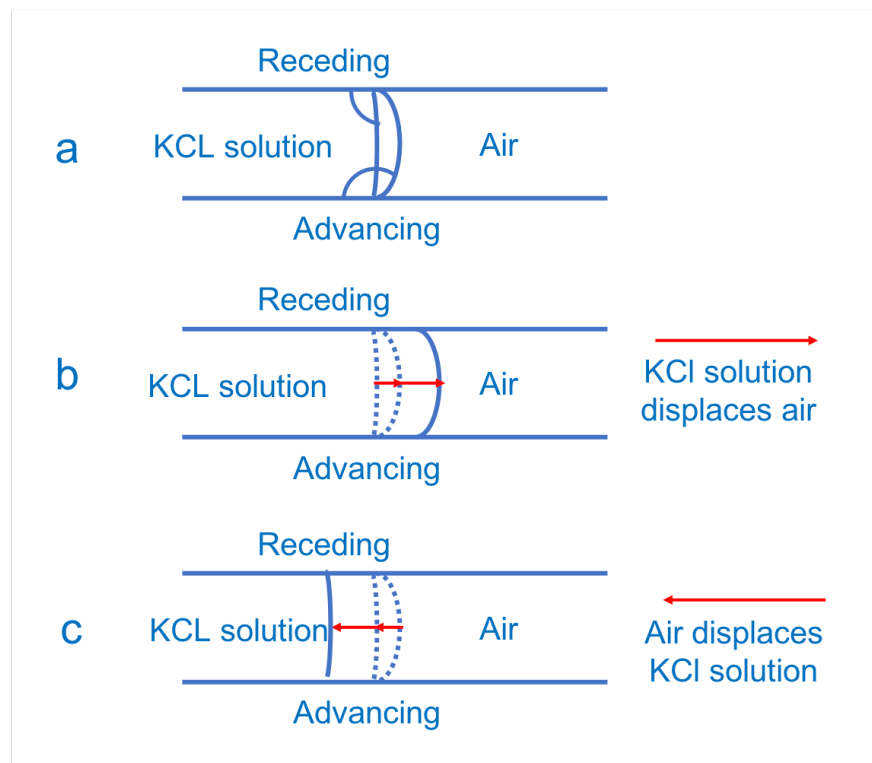


Figure 4- 3 Explanation of how EWOD works with advancing and receding contact angles

With the application of EWOD, one of the contact angles suddenly decreases (see section 4.2.2), causing an instant inequilibrium. To reach another equilibrium, with interface remained unmoved, the other contact angles increase. When the other contact angles reach the advancing, the fluid continues to move with a pressure difference still exists. See details in Figure 4.3.

For the green line and blue line, before equilibrium, displacement of KCl solution by air was done. The contact angle was equilibrium at receding. With the application of EWOD, one contact angle suddenly decreased, and the other contact angles increased and the interface reached another equilibrium with interface unmoved. The sudden change of blue line was due to a sudden change of other contact angles.

For the black line and red line, with EWOD applied, the other contact angles first turned into advancing. However, pressure difference still existed and the interface started to move. With higher pressure difference, the red line moved faster and further.

4.2 Capillary Pressure – Saturation Hysteresis in a Wedge-Shaped Channel

Hysteresis is commonly observed in the capillary pressure and saturation relationship from multiphase flow experiments in porous media. Rather than being a single-valued function, this relationship depends upon the history of imbibition and drainage (see introduction).

Hysteresis is affected by pore geometry and the associated with the asymmetry of imbibition and drainage. According to Jerauld and Salter [*Jerauld and salter*, 1990], aspect ratio and pore-to-pore size correlation dominate the observed hysteretic behavior in multi-phase fluid displacement in porous media.

In this section, hysteresis measurements were performed at no voltage/with voltage conditions to compare the difference in imbibition and drainage scans for the same channel geometry but for different contact angles.

4.2.1 Imbibition and Drainage Scans

During an experiment, when no voltage was applied, the liquid phase pressure was modified by adjusting the height of the micrometer. An initial pressure step of 20 Pa was applied and pressure increment of 10 Pa were used. The channel was initially fully saturated with the liquid (KCl solution).

When no voltage is applied, air phase is the wetting phase. First, an imbibition scan was performed by decreasing the pressure at liquid side to enable air to invade the channel and displace the liquid. When the channel was (almost) fully saturated with air, a drainage scan was performed by increasing the pressure on the liquid such that the liquid would invade the channel.

The same experiment was repeated but with an applied voltage of 500 V to alter the contact angle. The channel was initially saturated with liquid (KCl solution) followed by an imbibition scan and then by a drainage scan.

In the channel with and without voltage, similar pressures are observed for the imbibition scans at the same saturations when no voltage/with voltage (Figure 4.4). However, in the drainage scans, a pressure difference of 10 – 20 Pa was observed between the voltage off and voltage on conditions (Figure 4.5).

In Figure 4.6, a comparison of saturations with/without voltage applied at the same pressures for drainage scan are shown. The saturations are very different. The saturation increases as the air phase changes from being the non-wetting phase to the wetting phase after voltage is applied.

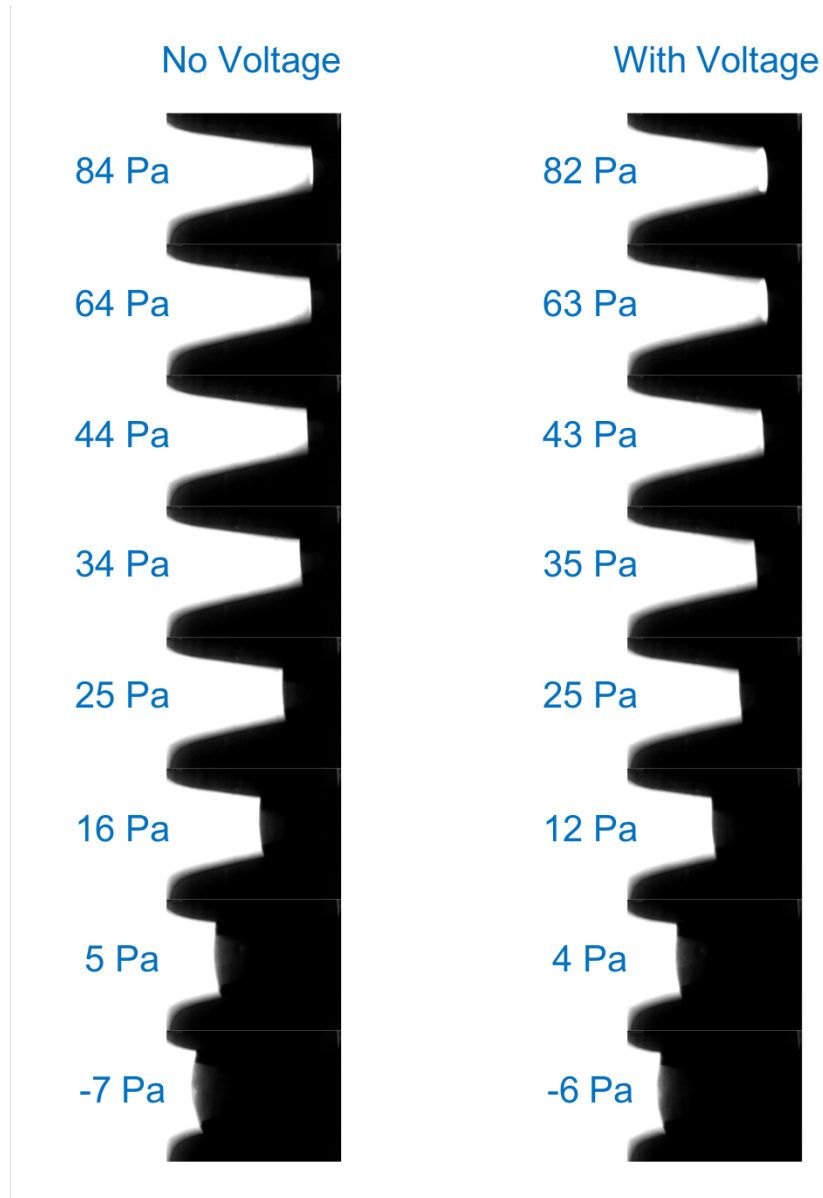


Figure 4- 4 Images of channel before (left) and after (right) applying voltage for an imbibition scan. In the imbibition scan, the no voltage and voltage conditions have similar hysteresis relationship between pressure and saturation of wetting (air).

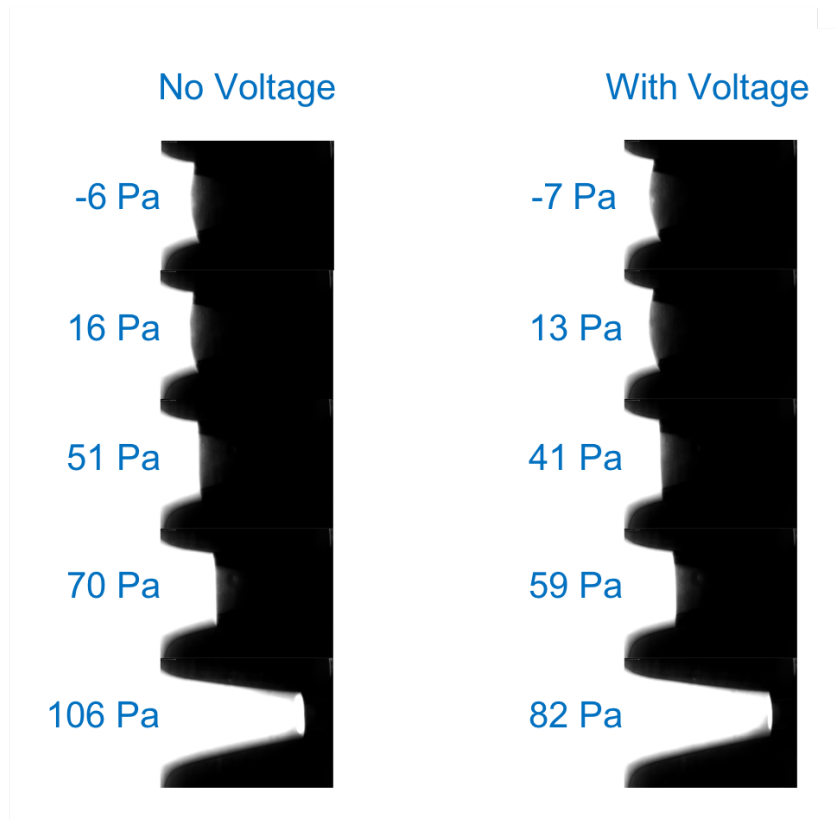


Figure 4- 5 Images of channel before (left) and after (right) applying voltage for the drainage scan. When the interface equilibrated at similar positions in the channel, the pressure with voltage applied differs from the no voltage condition. There was a difference of 10 - 20 Pa for similar saturation of wetting (air).

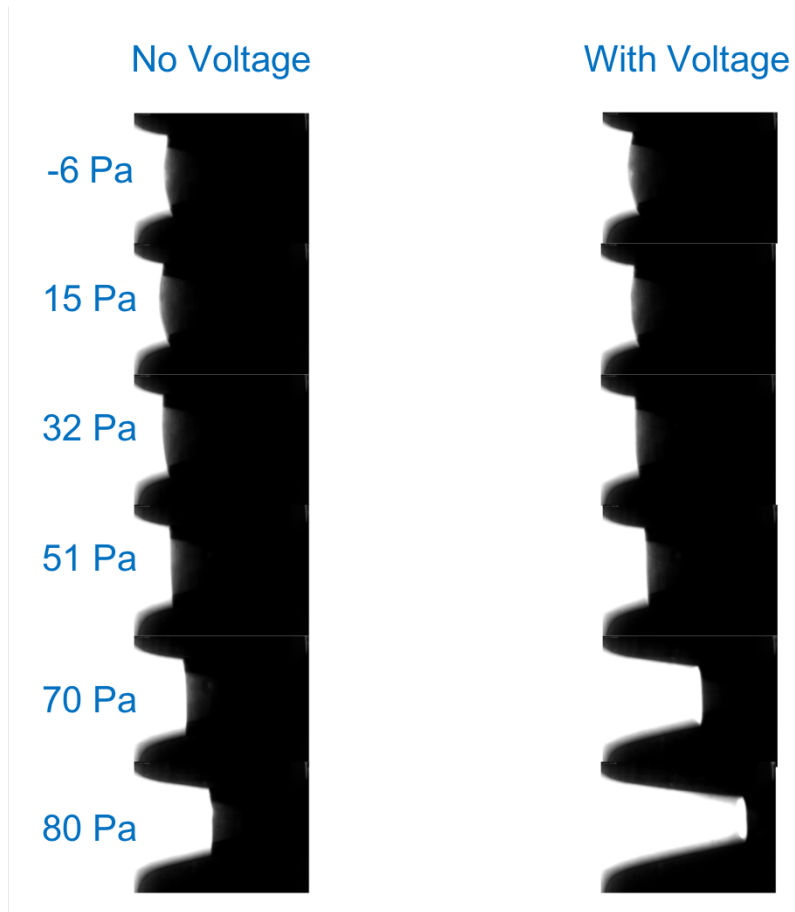


Figure 4- 6 The comparison of saturations with/without EWOD at same capillary pressures.

By recording the pressure and saturation of wetting (air) for every step, a hysteretic relationship was observed between the two voltage conditions. The hysteretic relationships are shown in Figure 4.7 and repeatable.

The explanation of the differences between the imbibition and drainage scans will be discussed in section 4.2.3.

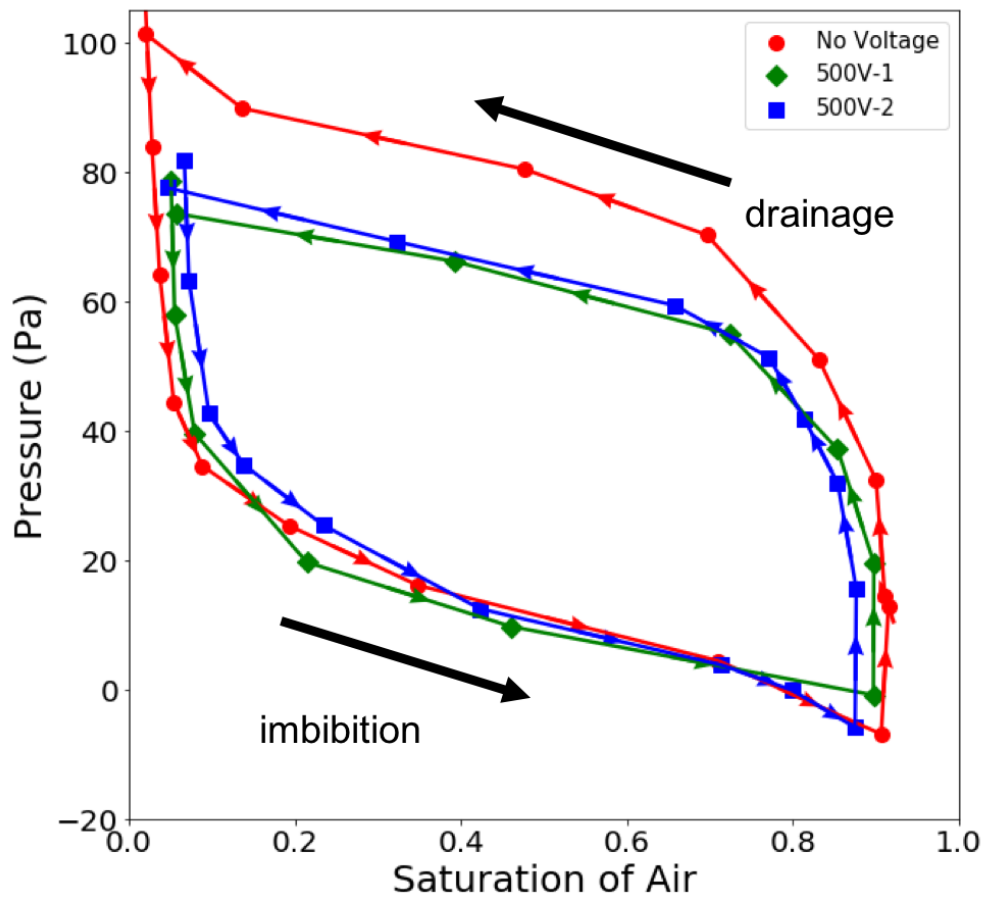


Figure 4- 7 Hysteresis loops for no voltage condition (red) and voltage conditions (green & blue). At the imbibition scan, the loops were almost overlapped and at the drainage scan, two loops have a pressure difference of 10 - 20 Pa.

4.2.2 X-Ray Scan

To investigate the change in contact angles before and after applying EWOD, X-ray scans were performed for two conditions. The X-ray images before and after applying voltage are shown in Figure 4.8.

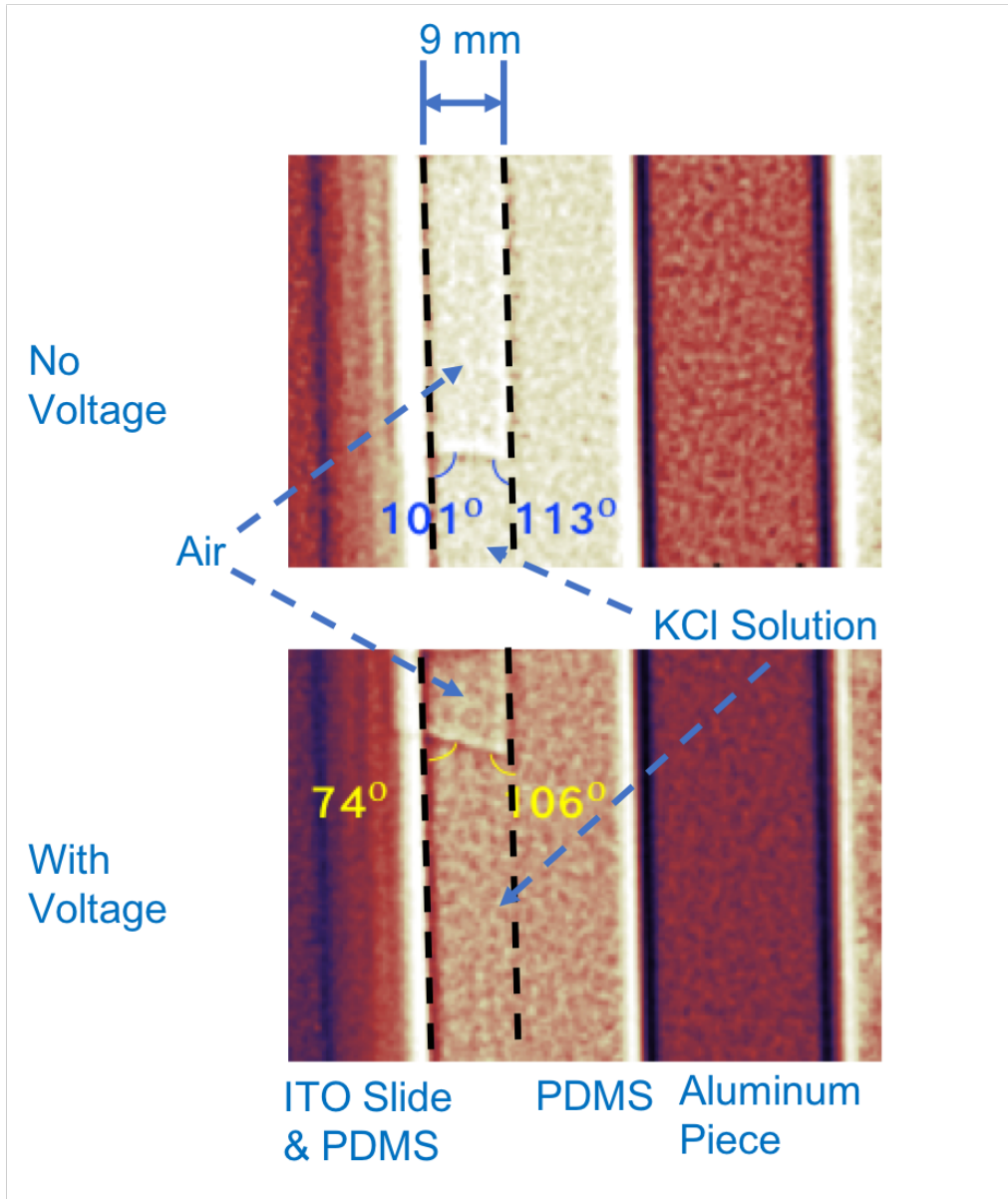


Figure 4- 8 X-ray scan of KCl solution in wedge-shaped channel for no voltage/with 500 volts. Before applying the voltage, the liquid phase was near the inlet (downside). The contact angle was about 100° between the liquid and PDMS for both ITO slide and Aluminum piece sides. When 500 volts was applied, the liquid/air interface was pushed into the outlet (upside) and only the contact angle near the ITO slide side was changed greatly to about 75°.

In Figure 4.8, with the application of the EWOD, the liquid/air interface moved toward the outlet. The contact angles changed from 101° and 113° to 74° and 106° for ITO slide side and Aluminum piece side, respectively.

When the micro-model was fabricated, the thickness of PDMS at Aluminum piece side was ~ 1 mm, which is much thicker than that at ITO slide side (~ 10 μm). Based on Equation 1.28, as the thickness of dielectric increases, the effect of EWOD decreases. This is the reason why only the contact angle on the ITO slide decreased significantly.

In section 3.2, it was mentioned that both the contact angles at top and bottom are changed significantly. In that case, it was able to make both the PDMS layer very thin. As one contact angle changed, same effect was observed (the interface moved forward).

4.2.3 Imbibition vs Drainage

As shown in section 4.2.1, with the application of EWOD, the imbibition scan and drainage scan exhibited very different behaviors compared with no EWOD conditions. In the imbibition scan, the hysteretic relationships of capillary pressure and saturation with/without EWOD almost overlapped. While for the drainage scan, with the same saturation, when EWOD was applied, the capillary pressure was typically less than that without EWOD applied. The difference was about 10 – 20 Pa.

Examination of images from these experiments help to understand this behavior. As observed in Figure 4.9, in the imbibition scan, air was displacing the KCl solution. For the no voltage condition, a typical contact angle in imbibition scan was $\sim 90^\circ$. As for the drainage scan, the contact angle was $\sim 120^\circ$.

In section 4.2.2, under the X-ray scan, it was observed that, with the application of EWOD, the contact angle was changed from $\sim 110^\circ$ to 74° .

Different behaviors observed between imbibition and drainage scans with/without EWOD are attributed to different contact angles on the top and bottom surfaces of the channels. In the imbibition scans for the same saturation, with and without applying voltage, the contact angle near the ITO slide changed from $\sim 90^\circ$ to $\sim 74^\circ$. While in the drainage scan, with and without EWOD at the same saturation, the contact angle changed from $\sim 120^\circ$ to $\sim 74^\circ$. This was not observable from the optical imaging performed during the measurements but from the X-ray image of the channel shown in Figure 4-8. A conceptual sketch is given in Figure 4.10 for a side view of the channel.

Using equation 1.56, an estimation was performed of the expected pressures. Based on the equation, the pressure differences for the imbibition and drainage scans with/without voltage were 60 Pa and 20 Pa, respectively. Compared to the experimental results, there is a factor of 3 in the pressure difference between the imbibition and drainage scans as oppose to a factor 5 observed in the experiments. Potential explanations include the possibility that the contact angle of 74° was not obtained with directly applying EWOD to the channel, but may be different. Second, equation 1.56 applies to a spherical fluid-fluid interface. In this case, with the application of EWOD, the interface is not spherical as the contact angles on the sides of the channel differ from those on the top and bottom, which all differ from each other. The equation needs to be re-derived for a mixed wettability condition.

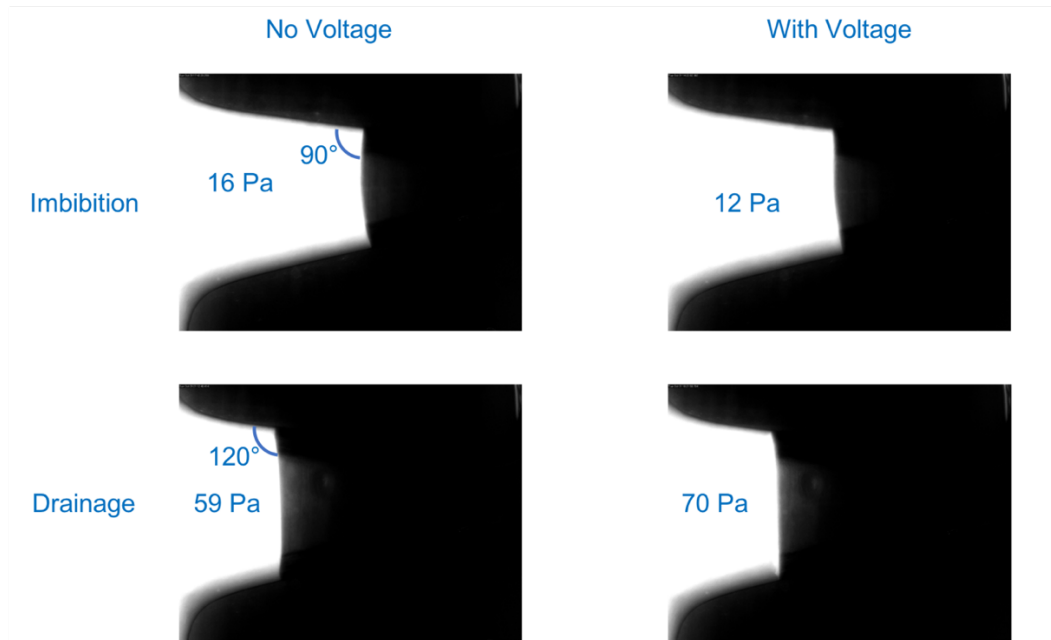


Figure 4- 9 Comparison of imbibition and drainage before/after EWOD. The white regions are fluid.

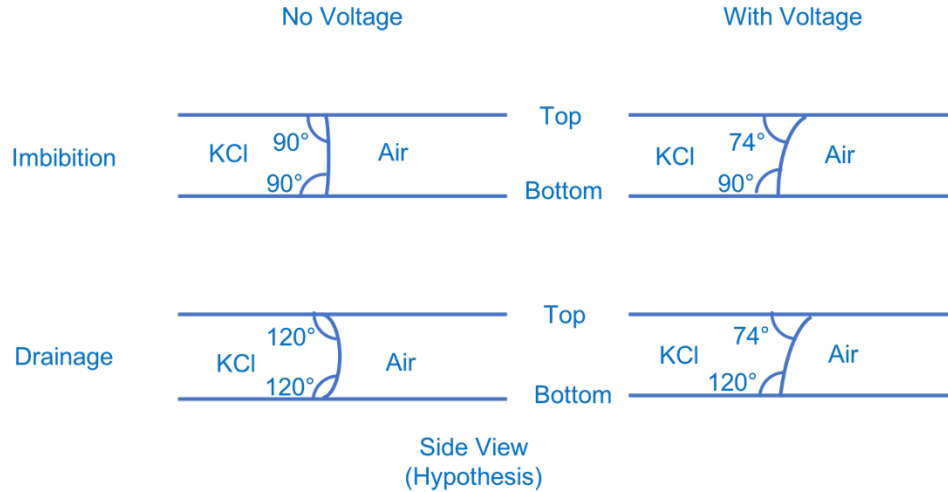


Figure 4- 10 (Hypothesis) Side view of contact angle changes in imbibition and drainage.

4.3 Pinning of Energy in Step-Channel

In section 4.1.1, local pinning of energy that arises from the roughness of a channel was observed. To explore the pinning and depinning of energy with/without the application of EWOD, we designed a step-channel to amplify pinning.

4.3.1 5-Step Channel

A wedge-shaped micro-model with 5 steps is shown in Figure 4.11. In the channel, the inlet and outlet are 2 mm and 0.5 mm, respectively. The distance from the inlet to outlet is 4 mm. 5 equal steps of 0.8 mm x 0.2 mm form a stair-shaped rough channel. The aperture of this micro-model is 0.9 mm.

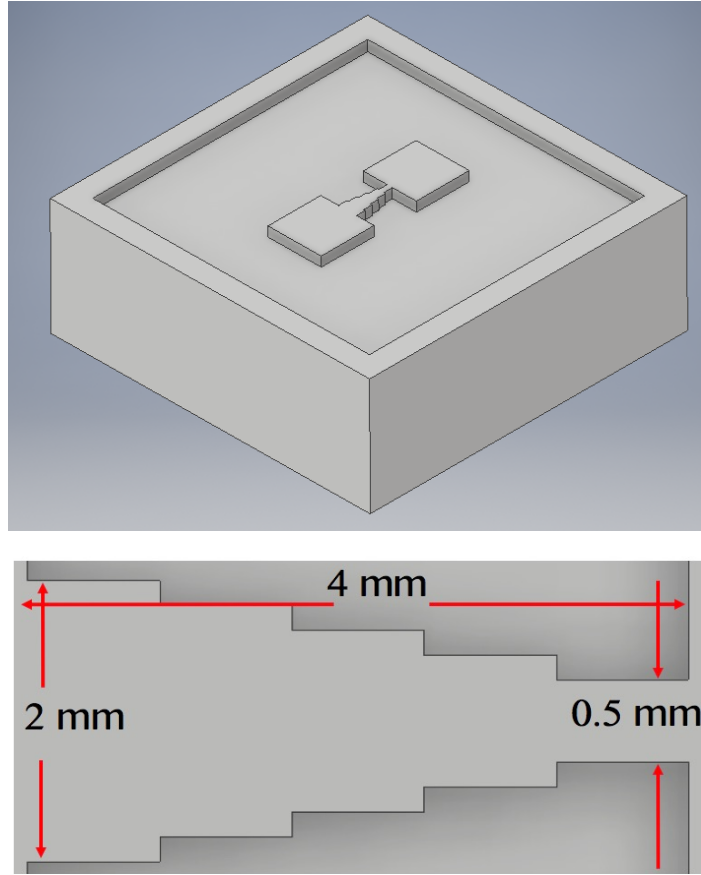


Figure 4- 11 The mold for 5-step channel in Inventor. The inlet and outlet are 2 mm and 0.5 mm, respectively. The channel cross 4 mm. The channel has five equal steps from inlet to outlet.

After setting the position of the KCl solution-air interface, the EWOD was switched on after 5 – 10 min to ensure the fluid-air interface was in equilibrium. Starting from almost the same initial saturation position (Figure 4.11), EWOD was applied under different pressures (70, 80, 90, 100 Pa). After 30 min, the voltage was turned off. The development of saturation is shown in Figure 4.12 and Figure 4.13.

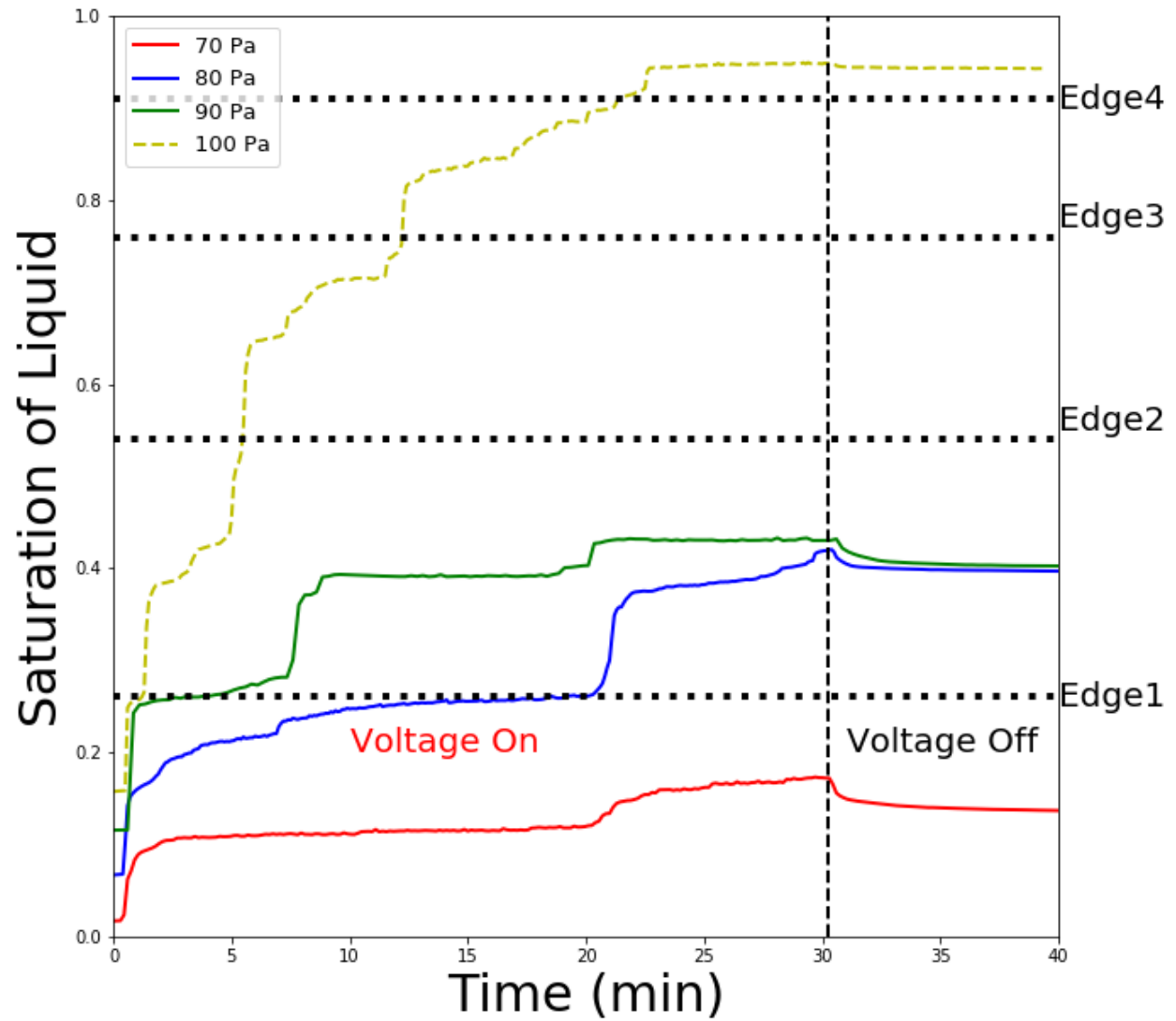


Figure 4- 12 The change of saturation of fluid with time after applying voltage to 5-step channel under different pressures.

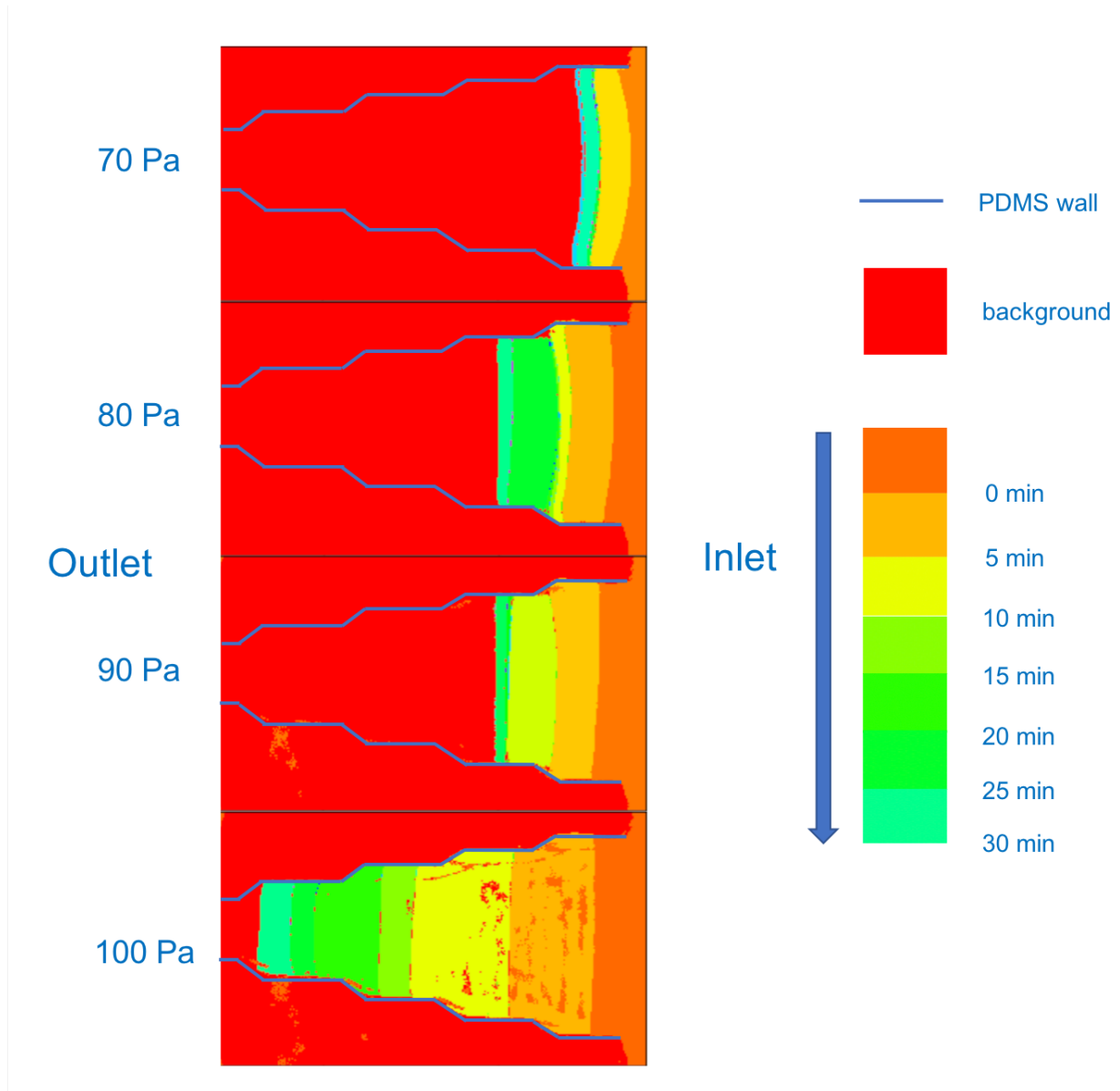


Figure 4- 13 Development of fluid-air interface in the 5-step channel with time.

For all experiments, immediately after applying EWOD, the interface started to move forward towards the outlet. Within 30 min, the interface reached an equilibrium state. When the voltage was turned off, the interface relaxed immediately but remained at almost the same position. The experiments were repeatable.

At 70 Pa, during the experiment, the interface never advanced past the first step. Some small jumps are observed that correspond to release of energy of ~ 30 nJ.

At 80 Pa, immediately after application of EWOD, the interface quickly reached the corner between the first and second steps. The interface was held there for some time then entered the second step abruptly. The released energy was about 40 nJ.

At 90 Pa, the behavior is similar to that at 80 Pa, the interface quickly moved towards the outlet until it reached the first corner. Compared with at 80 Pa, the interface was held for a shorter period of time before release. The released energy was about 60 nJ.

At 100 Pa, the interface was able to cross all the corners and reached the last step. The maximum pinned energy was about 100 nJ between the 1st and 2nd steps, 90 nJ between the 2nd and 3rd steps, 40 nJ between the 3rd and 4th steps and 17 nJ between the 4th and 5th steps.

Some conclusions were obtained with above experiments. First, the maximum pinned energy for each experiment occurred immediately after applying EWOD. At higher pressures, the maximum pinned energy tended to be larger, and the pinning time tended to be shorter than at lower pressures. The depinning energy decrease as a fluid-fluid interface progressed through the channel.

4.4 Local and Remote Wettability

In the previous experiments with wedge-shaped channel, EWOD was applied to the entire channel. In section 3.2, with the application of EWOD on the middle electrode, it was demonstrated that droplet could be transported toward a region with applied voltage. From this inspiration, a new question was raised: How far does the EWOD effect extend past an active electrode? Does it disappear immediately when the interface passes the active area or can it still affect fluid-fluid interface? See Figure 4.14 for a full explanation of the questions.

To answer those questions, I used wedge-shaped micro-models with discrete electrodes to investigate the local and remote effect of EWOD.

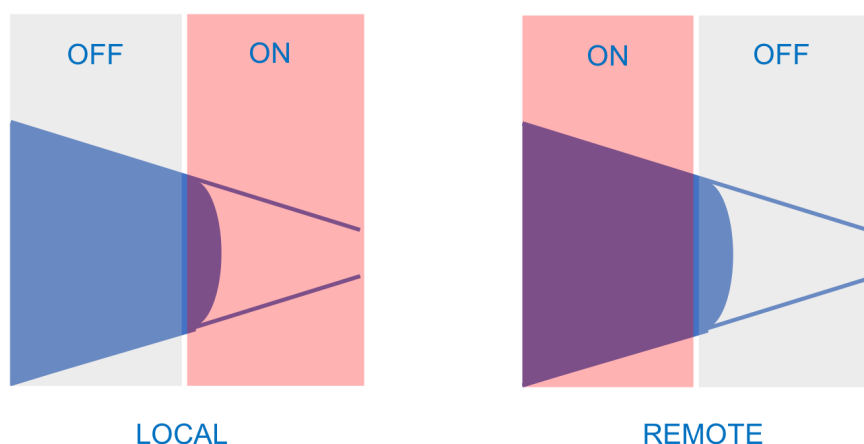


Figure 4- 14 Explanation of local and remote EWOD in a 2-electrode sample. In both figures, the interface is resting at the same position. In the left figure, the left electrode is off and the right electrode is on. EWOD is directly applied to the interface. This is called local EWOD. In the right figure, the left electrode is on and the right electrode is off. There is no direct effect of EWOD on the interface. But EWOD is still applied on the liquid. This is called remote EWOD.

4.4.1 Fabrication of Micro-Model with Discrete Electrodes

In section 2.1.3, I A complicated method is described that I developed to fabricate a slide with discrete electrodes. In that section, the metal used was silver. Unlike the condition there, in the fabrication of micro-model, we used an ITO slide where the entire surface is coated with ITO. In Chemistry, ITO etching is commonly performed with HCl + Zn powder. However, in our lab, I was not able to etch the exact desired area. Besides, there was a crucial disadvantage. The ITO slide is transparent. When etched by chemicals, an optical camera could not distinguish between etched and unetched regions, making it impossible to see the electrode.

In considering this, I developed a simple method to create discrete electrodes on ITO slide. After arranging the electrodes, a diamond knife was used to create parallel slits to separate the electrodes. The resistance across the adjacent electrodes was measured with a multi-meter to ensure that the electrodes were disconnected. Following the same steps as in section 2.2, a micro-model was fabricated with discrete electrodes.

With this method, a micro-model with 2 electrodes was made to test local versus remote EWOD effects. The pattern of the micro-model is shown in Figure 4.15.

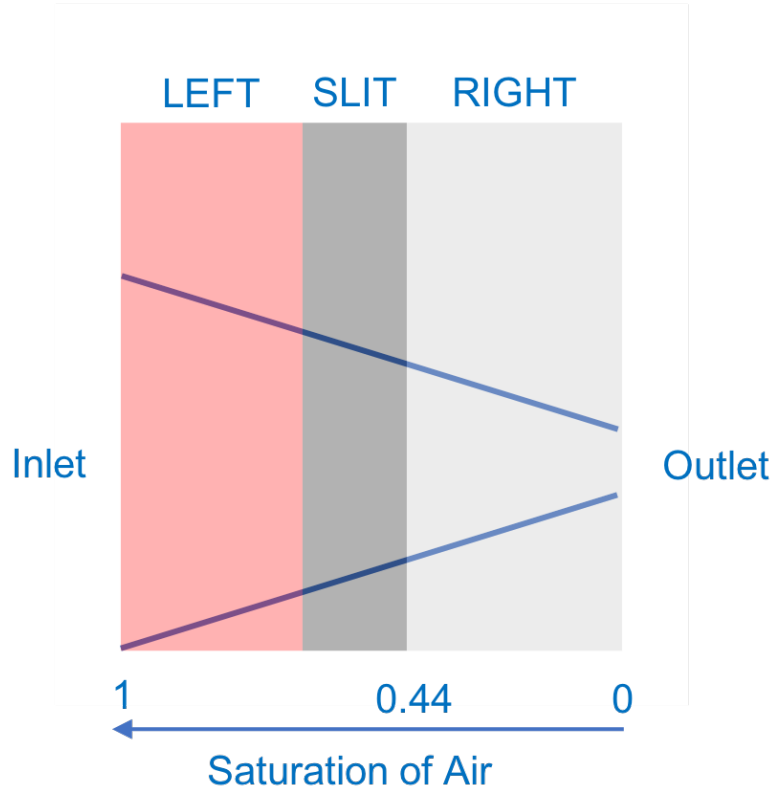


Figure 4- 15 A two-electrode micro-model fabricated by creating slits in the coating of the ITO slide. In this sample, the left electrode crosses channel saturations of 0.44 to 1 and the slit + right electrode is for channel saturations of 0 to 0.44 based on the saturation of air. The inlet represents a saturation of 1 and the outlet represents 0.

4.4.2 Hysteretic Experiments

With this sample, I first investigated $P_c - S$ hysteresis for the no voltage condition and with only the left electrode on. A set of experiments was performed and the results are shown in Figure 4.16.

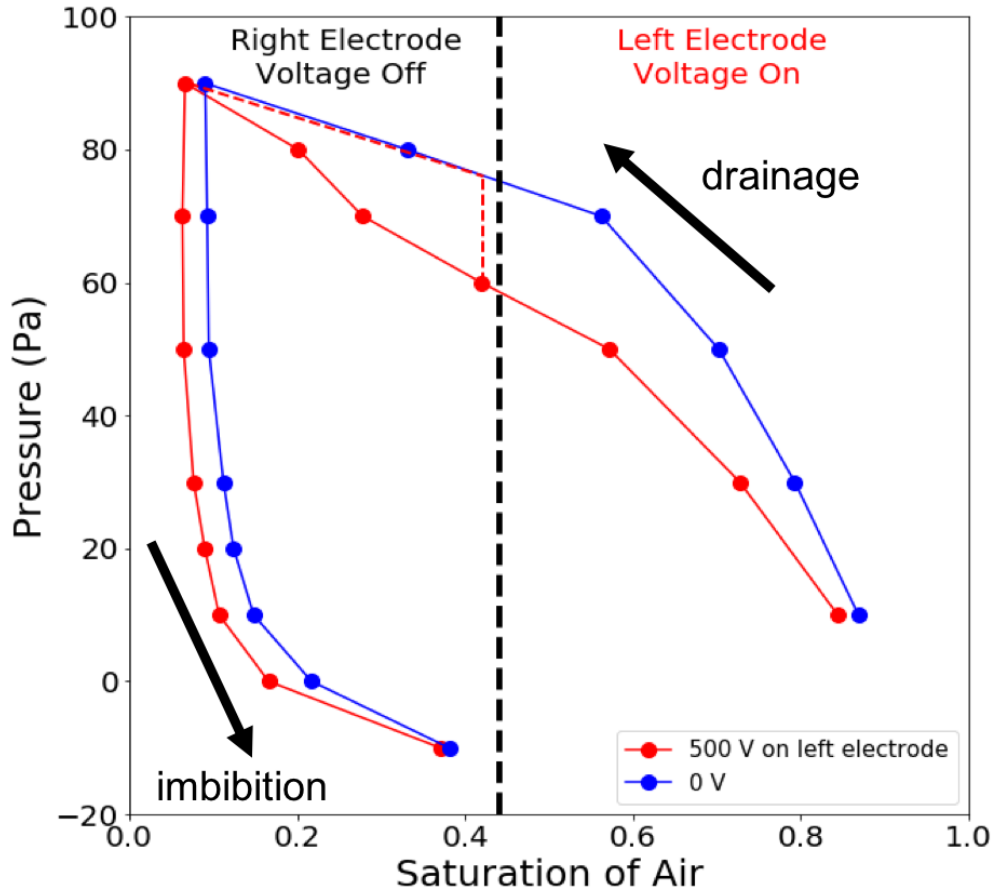


Figure 4- 16 Hysteresis relationship between pressure and saturation for the 2-electrode sample. The solid lines are real routes. The blue line represents the loop with no EWOD applied. The red line corresponds to the one with left electrode on. The dashed red line proposed an imaginary route for the red loop if remote EWOD had no effect on the interface.

Both experiments started with drainage scan. With/without EWOD applied, the interface was at equilibrium near the inlet. Since the saturation of air was tracked, the saturations were close to 1 at the beginning of the experiment. The electrode spanned the channel that is fully or partially saturated for air saturation values from 1 to 0.44. When the interface was still on the active electrode, comparison of the drainage scans with/without EWOD show a difference of 10 – 20 Pa, which is similar to the results in section 4.2.

When the interface crossed the active electrode and rested on the inactive electrode, the capillary pressure and saturation relationship started to differ from that shown in section 4.2. In Figure 4.16, a dashed red line is shown: If the effect of EWOD disappears when the interface is no longer on the active electrode, the relationship between capillary pressure and saturation should immediately collapse to the no EWOD condition. However, that was not observed. The solid red line gradually merged to the blue line from the no EWOD case at an air saturation of ~ 0.1 .

The experiment was repeatable. With these results, it can be concluded that, even though the interface passed the active electrode, the effect of EWOD does not disappear immediately. Instead, the effects of EWOD decreased gradually with distance. To see a direct comparison between local and remote effects of EWOD, additional experiments were performed that are described in the next section.

4.4.3 Control Experiments

With the same sample, some control experiments were performed on two samples. Sample (s1) was the same as experimented in section 4.4.2. Sample (s2) was fabricated with same method. For each set of experiments, the interface was initially resting on similar position in the area above the right electrode under the same pressure. Left or right electrode was turned on for 30 min. The change from initial interface to final interface were shown in Figure 4.17. The KCl solution phase in the channel before EWOD is in dark purple and the changed area of KCl solution phase is marked as yellow. The extraction of each sections is imperfect due to the existence of the slit and shadowing. Raw images are given as a supplement.

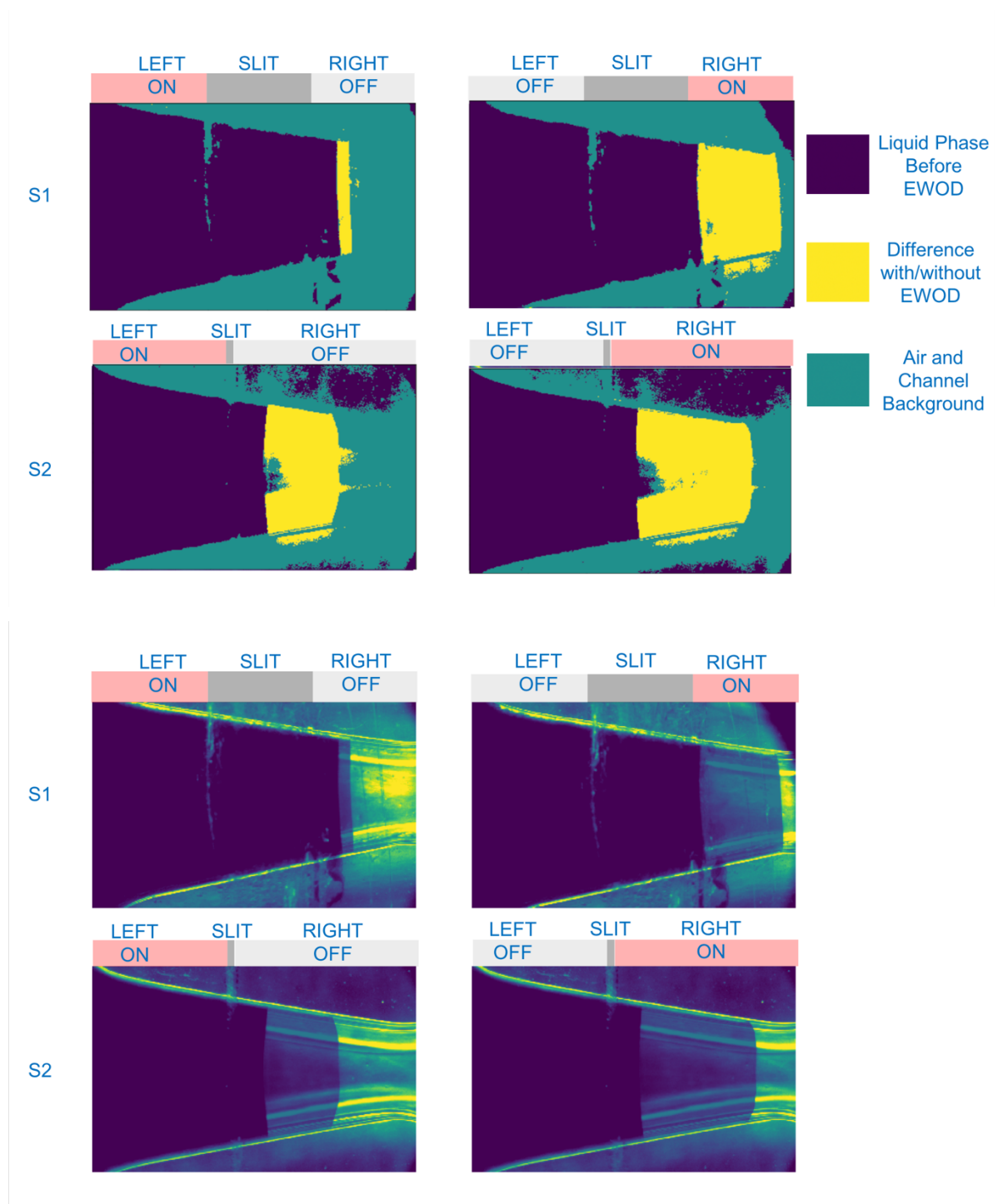


Figure 4- 17 Control experiment results for two samples. From the results, when EWOD was performed remotely, it still affected the interface (the interface still moved). However, this effect was much weaker compared to local effect.

For sample 1, when the left (remote) electrode was turned on, in 30 min, the interface moved a much shorter distance, compared with the condition when right (local) electrode was turned on. With sample 2, without the wide slit, I initialized the interface very near to the left electrode. This time, the effect of remote EWOD was stronger.

In conclusion, when EWOD is applied remotely, its effect doesn't disappear immediately. Instead, this effect gradually weakens with the distance from the interface to the active electrode. Initially, the remote effect was attributed to either fringing effect or changes in solid-liquid interfacial tension above the active electrode, or from floating potentials of electrodes. In a follow-on experiment, when voltage was applied to a remote electrode, an attempted was made to ground the other electrodes. This shorted out the sample. This suggests that the remote effect was caused by the floating of electrodes. Even though every electrode is separated, by applying a voltage to one electrode, the nearby electrodes are at some non-zero voltage that causes the fluid-fluid interfaces to move though far from the "active" electrode. Additional work is needed to confirm these observations.

4.5 Multi-Cylinder Channel: Reconnecting Isolated Droplets to Main Fluid

In previous sections, results from an investigation were presented on the effect of EWOD in wedge-shaped channels. From the results, the application of EWOD to manipulate contact angles cause fluid-fluid interfaces to move, thus changing the saturation and interfacial area. Our goal was to try to connect isolated droplets using EWOD as another method to study the effect of changing IAV by merging drops, and the effect on pressure while the saturation remained the same. In a wedge-shaped channel, isolated droplets were difficult to create. A sealed sample with multiple cylinders, commonly used by other researchers [Dye, *et al.*, 2016], was fabricated to drive isolated droplets, and make it have more similarity compared to real porous media.

4.5.1 Fabrication of Multi-Cylinder Sample

In section 2.2, the fabrication of wedge-shaped micro-model with EWOD setup was introduced. Here, a similar procedure was used to fabricate the multi-cylinder sample. In this sample, discrete electrodes were also created by the method described in section 4.4.

The mold of the multi-cylinder channel is shown in Figure 4.18. A 6 x 6 cylinder-matrix is set within an area of 15 mm x 15 mm. The diameter of each cylinder is 2 mm. Two adjacent cylinders have center distance of 2.5 mm.

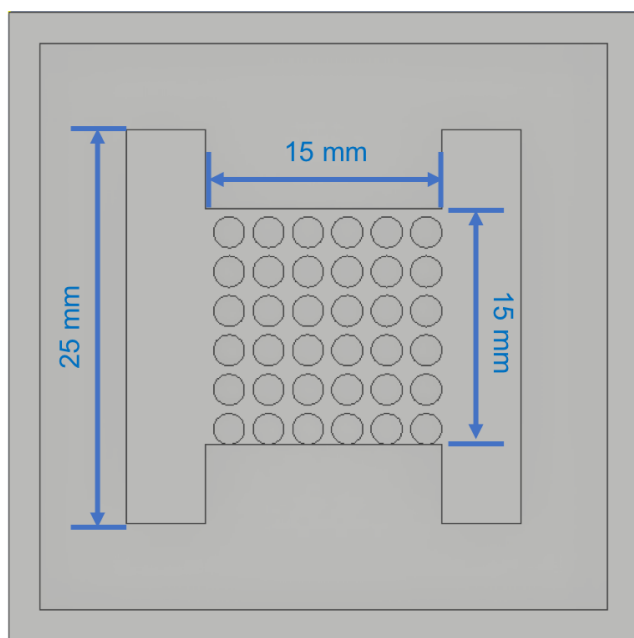


Figure 4- 18 Mold for fabricating sample with multiple cylinders. Thirty-six cylinders with diameter of 2 mm are within a square of 15 mm x 15 mm. The distance between adjacent centers is 2.5 mm.

4.5.2 Experimental Setup

When experimenting with multi-cylinder channel, a CCD camera + microscope could not be used to record the development of the fluids because this channel was much larger and the entire channel could not be completely recorded while under a 5x objective. Instead, a raspberry pi camera attached to a lightboard was used to obtain the images. Meanwhile, KCl + fluorescent dye was replaced by 0.3M NaCO₃ + Bromocresol green to increase the contrast of the liquid solution. The new setup is shown in Figure 4.19.

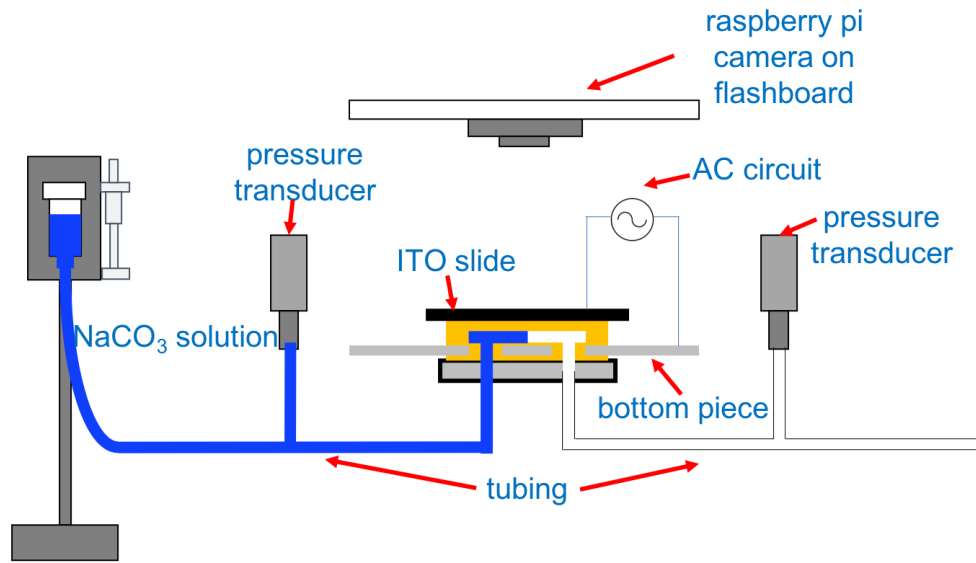


Figure 4- 19 Experimental setup for the multi-cylinder sample. To record this channel with much larger view, we used a raspberry pi camera sticking on a flashboard. We also used 0.3M NaCO_3 with small amount of Bromocresol green to enhance the liquid in the images.

4.5.3 Reconnecting

From invading and withdrawing liquid from the multi-cylinder channel, some liquid became trapped within the pore structures in the channel. In Figure 4.20a, the liquid on left (circled by red) is isolated from the main liquid. Then EWOD was applied for 10 min on the electrode as marked. As shown in 4.20b, the main interface moved forward and connected with the isolated liquid. In the meantime, it trapped some air (circled by blue). As the voltage was turned off, the interface did not change significantly (Figure 4.20c).

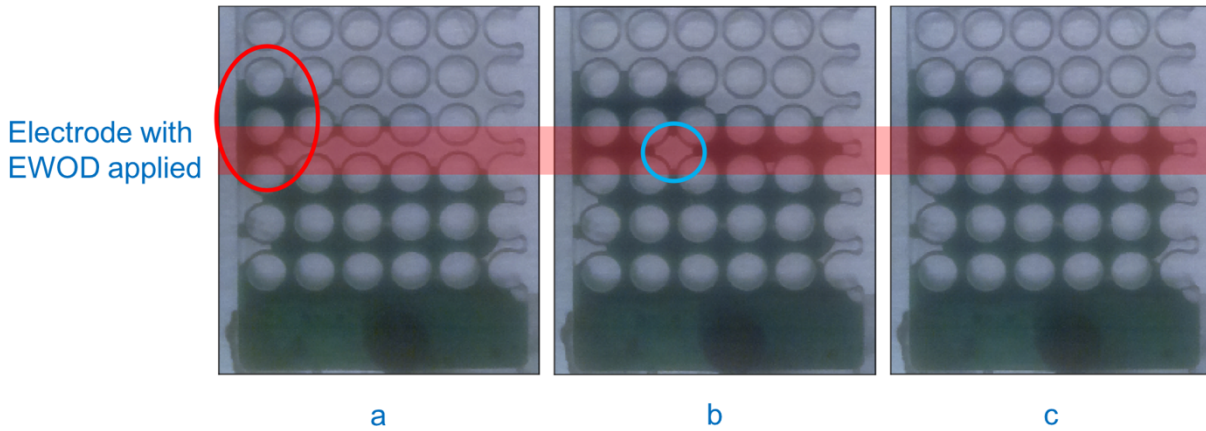


Figure 4- 20 image of multi-cylinder channel with reconnecting isolated droplets to main fluid:
a) before EWOD b) with EWOD c) after EWOD.

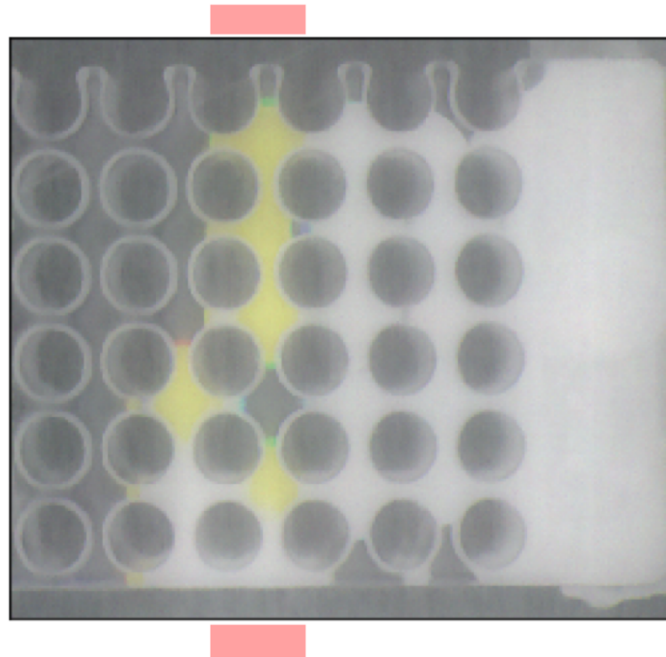


Figure 4- 21 To make the difference among three images outstanding, we use image of before, with, after EWOD to compose the Blue, Green, Red pixel of this figure, respectively. In addition to the change of main interface (yellow), we also observed some small change of interface with/without applying EWOD.

In Figure 4.21, it can be seen more clearly. Initially, the main fluid and the isolated fluid were shown in white. Both of their interfaces were at the electrode area. With applied voltage on the electrode, the main fluid started to move towards left and connected to the isolated fluid. The yellow + green was the area difference before/after EWOD. By turning off the voltage, the contact angle between PDMS cylinder and fluid decreased, causing the area difference of green. To maintain the constant volume, the interface moved out (red area). Due to the low resolution of raspberry pi camera, it was unable to extract the contact angles.

CHAPTER 5. SUMMARY AND FUTURE DIRECTIONS

EWOD is a method to create a pressure difference by manipulating the contact angle among a fluid-fluid-solid system with an electric field on a dielectric. In a single-plate setup, by comparing different materials, frequencies and molarities, it was found that the dielectric properties of PDMS, an AC frequency of 50 Hz and molarity of 1M KCl solution was the best combination to perform EWOD experiments. In a double-plate setup, EWOD was performed to transport and merge droplet(s). During the application and withdrawal of EWOD, contact angle alternation was observed.

In previous work on two-phase immiscible flow system, the manipulation of saturation was achieved by externally controlling the capillary pressures, while EWOD was investigated using liquid droplets. In this work presents the first time that EWOD was embedded into a two-phase immiscible flow system with continuous fluids to internally change fluid saturations and contact angles.

As a very first step, a sealed micro-model with EWOD setup was needed. Traditional micro-model fabrication methods only focus on the aperture of the channel. For a micro-model with EWOD setup, in addition to the aperture, the thickness of the channel wall (dielectric layer) and conductivity of substrates must also be taken into consideration. Being aware of that, a novel method was developed to fabricate micro-models with an EWOD setup. In the new type of micro-model, one side of the channel has a thin PDMS wall ($\sim 10\ \mu\text{m}$) and ITO as conductive layer. While for the other side, the PDMS wall is much thicker ($\sim 1\ \text{mm}$) and an Aluminum plate is used as a ground electrode.

With this novel micro-model, in an open system (open to the atmosphere), the capillary pressure remained the same by applying EWOD onto the micro-model but the saturation did not. From an X-ray scan, it was observed that, by application of EWOD, only the contact angle between the fluid-fluid interface and the channel wall near the ITO side changed greatly from $\sim 110^\circ$ to 74° .

The mechanism of how EWOD affects the fluid-air interface is: a certain interface (in this experiment it was KCl solution – PDMS) is able to equilibrate at different contact angles. Among those contact angles, the smallest and largest are called receding and advancing contact angles, respectively. In this case, if the goal is to displace air by KCl solution, the pressure of the solution

needs to be increased. With slow increments in pressure, the interface won't start to move until the contact angle reaches the advancing value. Once it reaches the advancing angle, the interface will move with the advancing contact angle. Similarly, if KCl solution is displaced by air, by slowly decreasing the pressure of KCl solution, the contact angle will first reach the receding contact angle and then start to move at the receding contact angle.

By comparing the hysteretic relationships between capillary pressure and saturation with and without EWOD, a major finding was that, at the same saturation, for the drainage scan, there was a pressure difference of 20 Pa with/without EWOD. While for imbibition scan, there was essentially almost no difference in pressure with/without voltage (~ 4 Pa). Based on the X-Ray images, a hypothesis was proposed to explain the difference: In the imbibition scans, at the same saturation, with and without applying voltage, the contact angle near the ITO slide changed from $\sim 90^\circ$ to $\sim 74^\circ$. While in the drainage scan, with and without EWOD at the same saturation, the contact angle changed from $\sim 120^\circ$ to $\sim 74^\circ$. An estimation was performed by using equation 1.56. Based on the equation, the pressure differences of drainage and imbibition scans with/without voltage should be 60 Pa and 20 Pa, respectively, instead of 20 Pa and 4 Pa observed in the experiments. Work is needed to develop an equation for estimating pressure under mixed wettability conditions. The differences in the contact angles for side walls of the channel (EWOD not applied to these surfaces) and top and bottom plates (different thickness of PDMS) suggest that equation 1.56 is not applicable in its current form.

To amplify the effect of roughness of a channel on the energy of de-pinning fluids, a 5-step channel was fabricated. The maximum pinned energy for each experiment occurred immediately after applying EWOD. At high pressures, the maximum pinned energy released during the initial step was greater than at lower pressures and the pinning time was shorter. As an interface moved farther into the channel, the depinning energy decreased.

From micro-model with discrete electrodes in the channel area, another major finding was that, when interface passed the active electrode, EWOD was still in effect remotely. Compared to the local effect, where only the interface was on the active electrode, the remote effect of EWOD was weaker. As the distance between the interface and the active electrode increases, EWOD's remote effect decreases. It was proven by experiment that the remote wettability was caused by floating grounds on the other electrodes. When a remote electrode was turned on, even though

electrodes were separated, a local electrode was still at some non-zero voltage, which caused the remote effect, i.e. the movement of the interface.

Additional work is still needed to improve EWOD-embedded sealed micro-models and to use these devices in the study and manipulation of systems that contain two immiscible systems. First, the experiments in this work were performed in an open system. In an open system under constant head conditions with EWOD applied, the capillary pressure does not change. The system equilibrates to the constant head pressure though the saturation changes. Instead, if the system is sealed when EWOD is applied, a change in pressure should be observed. I attempted to seal the system and apply EWOD. However, the interface never reached equilibrium in the channel because of trapped air which is compressible. Better methods are needed to make close system that can achieve equilibrium.

Second, only static X-ray images of fluid-air-solid interfaces were recorded. Thus, it is hard to quantify the effect of EWOD on the relationship between capillary pressure and saturation. In this work, only one view of the contact angles was obtained and observed to change from $\sim 110^\circ$ to $\sim 74^\circ$. Full 3D X-ray imaging of fluids in the channel is required with and without EWOD. A difficulty is maintaining a constant temperature. If 3D information could be obtained from EWOD embedded sealed micro-models, then interfacial area per volume could be obtain for systems where the saturation was manipulated internally, instead of the tradition use ofl external pressures to change fluid saturations. In addition, the 3D information on the shape of the interface, especially in mixed wettability conditions, would enable derivation equations to estimate pressure for systems with multiple contact angles because of surface conditions. Also, it is worth investigating how EWOD affects advancing and receding contact angles as the impact of EWOD on the drainage and imbibition scans were observed to be significantly different.

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