## Electrohydrodynamics of surfactant-laden fluid-fluid interfaces

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### Abstract

Electric fields are integral to numerous industrial and scientific processes that involve multiphase complex fluid systems; for example, electrocoalescence, electro-emulsification and dielectrophoretic manipulation in microfluidic devices. In these processes, electric fields deform, break and coalesce fluid interfaces. These systems contain surface-active species, or surfactants, which simultaneously transport to the interface. To engineer the system response, the deformation, conditions for instability of the interface and the transport of surfactant under electric fields needs to be quantified. In this thesis, we analyze the response of liquid drops, and surfactant transport to interfaces under electric fields. The impact is prediction of drop behavior in devices and development of a unique tool to engineer and manipulate liquid-liquid interfaces.

We first employ boundary integral computations to highlight the role of convection of surface charges in the transition in breakup mode of a weakly conducting drop suspended in another weakly conducting drop, under a uniform electric field. Accumulation of surface charges at the tips of the drop results in an abrupt change from a breakup mode characterized by bulbous lobes to one distinguished by the formation of conical tips. We next model interaction between multiple conducting drops and disturbances in operating conditions as temporal fluctuations in the electric field. We use small deformation theory and the boundary integral method to predict the transient deformation and criterion for breakup of the drop under a random electric field. We demonstrate that fluctuations in the external electric field increase the average drop deformation, reduce the time for breakup, and soften the transition from steady state to breakup. We then probe the addition of soluble surfactants to the drop phase in terms of the effective viscosity of a dilute emulsion of such drops. Small amounts of added surfactant can greatly impact the viscosity of the emulsion for certain regimes of surfactant transport and depletion. We then proceed to develop an experimental platform to quantify the transport of surfactants to an oil-water interface under electric fields. We show that surfactants that form charge carriers in an oil phase show an enhanced transport under electric fields. Moreover, the field selectively affects surfactant transport in the oil phase. In summary, using theory, computation and experiment, we make significant contributions to underline the ability of electric fields to manipulate liquid-liquid interfaces.

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# Chapter 1

## Introduction

Liquid-liquid interfaces are subjected to electric fields in applications like electrospray mass spectrometry<sup>1,2</sup>, electrocoalescence<sup>3,4</sup>, electro-emulsification<sup>5,6</sup>, electrospinning<sup>7</sup>, inkjet printing<sup>8,9</sup>, structuring colloidal particles at interfaces<sup>10–12</sup> and microfluidic devices<sup>13–16</sup>. These systems typically comprise two immiscible liquids, along with surface-active molecules, called 'surfactants' which adsorb at the interface. Depending on the particular application, the interface may deform, coalesce or rupture under the applied electric field, while the surfactant molecules simultaneously transport to the interface. To achieve a desired electric field-induced effect, it is important to accurately predict the response of the interface to electric fields, and determine how the applied field impacts surfactant transport.

The response of liquid interfaces to electric fields falls under the purview of the fields of electrohydrostatics and electrohydrodynamics. If the two liquids are perfect dielectrics, or if one is a perfect conductor and the other a perfect dielectric, the electric field does not result in a fluid flow at steady state; the phenomenon is called 'electrohydrostatics'<sup>17–23</sup>. If both the liquids are weakly conducting, or 'leaky dielectric,' the applied field generates a sustained fluid motion at steady state, and the phenomenon is termed 'electrohydrodynamics<sup>23–27</sup>. From nearly a century ago, electric fields have been known to deform and rupture fluid-fluid interfaces<sup>17–19,21,22</sup>. Based on energy arguments, it was predicted that the interface would deform along the direction of the applied field into prolate shapes<sup>20</sup>; however drops of oil suspended in another oil were observed to deform perpendicular to the direction of the field, into oblate shapes<sup>21</sup>. This phenomenon was explained in 1966, in a seminal work by G. I. Taylor<sup>24</sup>. He formulated the 'leaky dielectric' model, where the oil phases were assumed to have a small, yet finite electrical conductivity. For small applied electric fields, Taylor predicted the condition where the drop would deform to a prolate or an oblate shape, from the interfacial stress balance condition. Subsequent work on electrohydrodynamics in the 60's and 70's involved experiments under constant and oscillatory electric fields<sup>25,27</sup>, and including higher order terms to Taylor's small deformation theory<sup>28</sup>. However, small deformation theory was not able to predict the deformation under larger electric fields, which were used in experiments; and research in this area slowed down a little.

The advance of computational power in the late 80's renewed interest in the area of electrohydrodynamics. Notably, the boundary integral method<sup>26</sup>, and the finite element method<sup>29,30</sup>, were widely used to predict large deformations and breakup criteria of drops under electric fields. This allowed comparison with experiments, and a reasonable agreement was found<sup>29,31</sup>. In recent years, a rigorous analysis of the transient deformation of a single drop under electric fields, accounting for different physical processes has been performed<sup>32–37</sup>. In particular, accounting for the convection of surface charges by the electrohydrodynamic flow resulted in a very good match between experiments and computations<sup>34</sup>.

The field of electrohydrodynamics received another boost in the early 2000's when microfluidic devices became popular. Electric fields have been incorporated in these devices to create, deform, sort and coalesce drops<sup>13–16</sup>.

More recently, electric fields have been employed to structure colloidal particles on drops<sup>10–12</sup>. In several of these applications, surfactants are added to bulk phases to create stable interfaces. Consequently, there has been an interest in modeling these interfaces in the presence of surfactants<sup>38–42</sup>. In the absence of an external field, the surfactant undergoes diffusion from bulk phases to the interface, and then an ad/desorption to/from the interface<sup>43–46</sup>. The intersection of electrohydrodynamics and surfactant transport is a rich, yet relatively unexplored field of research. There are several fundamental questions that need to be answered before a comprehensive model for electrohydrodynamics of surfactant-laden interfaces can be established. The objective of this thesis is to quantify the response of liquid drops, and surfactant transport to interfaces, under electric fields via theory, computation and experiment. The impact is a prediction of drop behavior in real devices, and development of electric fields as a valuable tool to precisely engineer and manipulate liquid-liquid interfaces and surfactant transport.

## 1.1 Background

#### **1.1.1** Drops under electric fields

Consider an uncharged, neutrally buoyant spherical drop of a fluid with initial radius  $a_0$  suspended in another immiscible fluid, as shown in Figure 1.1. The viscosity, permittivity and electrical conductivity of the fluids are denoted by  $\mu$ ,  $\varepsilon$  and  $\sigma$ , respectively; the subscript 'i' denotes properties of the drop phase fluid, and the subscript 'o' denotes properties of the medium phase fluid. When a uniform electric field of strength  $E_{\infty}^*$  is applied across this system, the interface of the drop acquires charge due to charge polarization. Further, there is a discontinuity in the distribution of electric field at the interface due to a mismatch in the electrical properties of the two fluids. Consequently, electric stresses are generated at the interface, which act to deform the interface. The electric traction acts in a nonuniform fashion along the interface. For small applied fields, the difference between the normal component of the electric traction in the medium phase and drop phase fluid  $\sim \cos^2 \theta$ . The traction is maximum at points called the 'poles' ( $\theta = 0, \pi$ ) of the drop, and vanishes at the 'equator'  $(\theta = \pi/2, 3\pi/2)$  of the drop. If a perfectly conducting drop is placed in a perfectly dielectric medium, the tangential component of the electric field,  $E_t^* = 0$ . When the drop and the medium are both perfect dielectrics, the interface does not acquire a charge under the electric field, hence the surface charge density,  $q^* = 0$ . Therefore, for a perfectly conducting or perfectly dielectric drop in a perfectly dielectric medium, the tangential component of the electric traction ( $\sim q^* E_t^*$ ) vanishes and the drop always deforms along the direction of the electric field into a prolate shape. There is no sustained fluid motion in the deformed drop; this phenomenon is termed electrohydrostatics<sup>17–23</sup>. An example of a conducting drop in a dielectric would be water drops suspended in an oil, which is prevalent in oil refining processes<sup>3,4</sup>. Dielectricdielectric systems are encountered in electrospinning of polymer melts<sup>7</sup>. For small values of the applied electric field strength, the steady deformation of the drop, defined as  $\mathcal{D} = \frac{L-B}{L+B}$  was calculated in 1962 by Allan and Mason<sup>21</sup>. For a conducting drop in a dielectric,

$$\mathcal{D} = \frac{9}{16} C a_E, \tag{1.1}$$

and for a perfectly dielectric drop suspended in a dielectric,

$$\mathcal{D} = \frac{9}{16} \frac{(S-1)^2}{(S+2)^2} C a_E.$$
(1.2)

Here,  $S = \varepsilon_i/\varepsilon_o$  is the ratio of permittivity of the drop phase to the medium phase fluid, and the dimensionless group  $Ca_E = a_0 \varepsilon_o E_{\infty}^{*^2}/\gamma$  is the electric capillary number, defined as the ratio of electric stresses to capillary stress, with  $\gamma$  denoting the interfacial tension between the fluids. The theory developed by Allan and Mason<sup>21</sup> holds when  $Ca_E \ll 1$ . The drop deforms to a spheroidal shape at this order.



 $\mu_o, \varepsilon_o, \sigma_o$ 

Figure 1.1: Schematic of the electric field induced prolate deformation of a drop. The axis of symmetry,  $\varphi$ , is along the direction of the electric field,  $E_{\infty}^*$ . The drop having viscosity  $\mu_i$ , permittivity  $\varepsilon_i$  and conductivity  $\sigma_i$  is suspended in a dielectric medium with viscosity  $\mu_o$ , permittivity  $\varepsilon_o$  and conductivity  $\sigma_o$ . The initially undeformed state of the drop is shown by the dashed curve. The semi-major and semi-minor axis of the deformed drop are denoted by L and B, respectively. The polar angle is denoted by  $\theta$ .

In practice, perfect dielectric systems ( $\sigma = 0$ ) are extremely difficult to find. Even the most insulating system is characterized by a small, measurable value of electrical conductivity due to the presence of impurities and trace amounts of water. For instance, the electrical conductivity of silicone oil and castor oil  $\approx \mathcal{O}(10^{-12} - 10^{-11}) \text{ S/m}^{21}$ . Some combinations of these fluids were observed to elongate along the equator of the drop into oblate shapes<sup>21</sup>. This observation was explained in 1966 by Taylor<sup>24</sup> in his 'leaky dielectric' model. He postulated that the weak conductivity of the fluids allow the interface to acquire charge under an electric field, which in turn gives rise to an electric traction having non-zero values for both the normal and tangential components. The tangential component of the electric traction is balanced by viscous shear stresses; thus a fluid flow is sustained in both phases even when the drop assumes a steady deformed state, and the phenomenon is called electrohydrodynamics. The deformation of the drop can be obtained from a balance between the electric, viscous and capillary forces acting at the interface, and for small applied field strengths, Taylor's small deformation theory predicts

$$\mathcal{D}_T = \frac{9}{16(2R+1)^2} \Big[ \frac{3R(3M+2)(1-RS)}{5(M+1)} + R^2(1-2S) + 1 \Big] Ca_E, \quad (1.3)$$

where  $M = \mu_i/\mu_o$  and  $R = \sigma_o/\sigma_i$ . Taylor's theory is, again, valid for  $Ca_E \ll 1$ , and predicts the drop deforms into a spheroidal shape: prolate if  $\mathcal{D}_T > 0$ , oblate if  $\mathcal{D}_T < 0$ .

Under larger electric fields, the deformation is nonlinear in  $Ca_E^{25-27,32}$ . Beyond a critical electric field strength, the drop undergoes an instability and breaks up into smaller drops. Two broad breakup modes have been observed<sup>32,33,47,48</sup>. In one mode, called 'end-pinching', the drop elongates to cylindrical shapes, which develop necks that detach from the cylinder and produce daughter drops having a size similar to the parent drop. The other mode, called 'tipstreaming' is characterized by the formation of pointed conical ends at the poles of the drop from which drops having size nearly three orders of magnitude smaller than the parent drop are ejected. Clearly, the size of the drops formed as a result of the instability depend on the breakup mode of the drop. Predicting transient deformation, breakup conditions, and the mechanism of breakup is important in applications to select an optimum operating condition; consequently a lot of advances have been made in this front through both experiments<sup>25,27,31,47,49,50</sup> and computations<sup>26,29,30,32–35</sup>. Among computational tools, the boundary integral method has been employed by several researchers to predict the transient, nonlinear deformation and breakup criteria of the drops<sup>26,32,34</sup>. This method works efficiently when the system can be described by a linear governing equation. The method involves rewriting the governing equations across the control volume into integral representations along the interface, hence reducing the dimensionality of the computational space by one<sup>51</sup>. It should be noted that although the governing partial differential equations are linear, the free boundary problem for the evolution of the interface is highly nonlinear.

An accurate prediction of the drop response requires careful analysis of the time scales for charging of the interface, establishing fluid flow and interface deformation. Recently, it was shown that the convection of the surfaces charges by the induced electrohydrodynamic fluid flow, a phenomenon called surface charge convection, needs to be taken into account for correctly predicting the experimentally observed transient deformation<sup>34</sup>. The role of this phenomenon in the breakup of 'leaky dielectric' systems has not been established previously. This has been addressed in Chapter 2 of this thesis.

Determining the response of a single drop to an electric field is important to understand the fundamental principles that dictate drop deformation and breakup; however this knowledge has limited relevance in practical systems. In applications like electrocoalescers and electro-emulsifiers, one deals with multiple drops which interact with each other, as well as with walls and system boundaries. Some studies have probed the effect of the interaction of two drops on their relative orientation in a uniform electric field<sup>52–54</sup>; however processes can be further complicated due to uncertainties like disturbances in operating conditions. Consequently, even when the applied macroscopic field, for example, the applied potential difference across the electrodes in an electrocoalescer, is steady, the drop response could be drastically different from that of a single drop or two drops under a uniform field. One strategy to model the behavior of these systems is to quantify drop response to a randomly fluctuating external field, an approach that has been widely adopted in predicting drop breakup and polymer extension in flow fields<sup>55–61</sup>. <u>An equivalent analysis for drops under electric fields is lacking</u>. We present this analysis in Chapter 3 of this thesis.

#### **1.1.2** Surfactant at interfaces

In recent years, the field of electrohydrodynamics has grown to encompass surfactant-laden interfaces<sup>37–40,42,47</sup>. Surfactant, or 'surface-active' molecules contain a hydrophobic part and a hydrophilic part. Due to their amphiphilic nature, when dispersed in a bulk phase, they migrate to the fluid-fluid interface to minimize the free energy of the system. The interfacial tension reduces due to surfactant adsorption. Surfactants are typically added to several processes to stabilize fluid-fluid interfaces, but can also be naturally present in other systems. For example, crude oil which is processed in electrocoalescers inherently contains waxes, resins and naphthenic acids, which act as surfactants and adsorb at the oil-water interface. In emulsification processes or microfluidic droplet based platforms, surfactants may be externally added to stabilize drops, or reagents like proteins and enzymes may also act as surfactants.

Surfactant transport from bulk phases to an interface follows a two step process<sup>43–46</sup>. Surfactant molecules close to the interface undergoes a reversible adsorption and desorption from the bulk to the interface. This reduces the local surfactant concentration near the interface, and surfactant in the bulk diffuses to the interface across the established concentration gradient. Upon surfactant adsorption, the interfacial tension of a fluid-fluid system decreases from the clean interfacial tension value in the absence of surfactants, to an equilibrium value which depends on the surfactant concentration in the bulk  $(C^*)$ , and the chemical nature of the surfactant and the two fluids. The concentration of surfactant at the interface,  $\Gamma$ , can be measured by determining the equilibrium interfacial tension as a function of the bulk surfactant concentration, using the Gibbs' adsorption equation,

$$\Gamma = \frac{1}{RT} \frac{\partial \gamma}{\partial \ln C^*},\tag{1.4}$$

where R is the universal gas constant and T is the temperature. The Gibbs' adsorption equation relates the two interfacial parameters ( $\gamma$  and  $\Gamma$ ) to a bulk parameter ( $C^*$ ). The relationship between  $\Gamma$  and  $C^*$ , known as the adsorption isotherm is used in conjunction with (1.4) to obtain the equation of state, which relates  $\gamma$  and  $\Gamma$ . Knowledge of the equation of state and the adsorption isotherm are necessary to model surfactant-laden interfaces under external fields.

The presence of surfactants at interfaces is known to have an influence on the breakup modes of drops under external flow fields<sup>62–66</sup>. The deformation of a surfactant-laden interface, and interfacial flows due to the external flow produce a nonuniform distribution of the surfactant at the interface. This generates tangential Marangoni stresses at the interface, proportional to the gradient in interfacial surfactant concentration. These extra stresses couple with the capillary stress and viscous stresses to affect the breakup conditions and breakup modes. An insoluble surfactant has been observed to facilitate the formation of pointed tips in drops under extensional flows, which then undergo breakup via tipstreaming. The size of the ejected drops depends on the initial surfactant concentration<sup>62,66</sup>. Surfactant gradients also allow the drop to be deformed to a larger extent before undergoing breakup, thus changing the critical condition for breakup<sup>62</sup>. Solubility of surfactants can lead to different observations for drops under flow fields, yielding results in between the limit of an insoluble surfactant and no added surfactant. The specific response depends on the initial surfactant concentration, and mechanisms of surfactant transport to the interface<sup>62,65,66</sup>. We discuss the effect of transport of surfactants in the rheology of a dilute emulsion of spherical drops containing soluble surfactant in chapter 4.

Under electric fields, experiments by Ha and Yang have shown that surfactants change the breakup mode from end-pinching to tipstreaming for a certain range in concentration; at concentrations outside this range, end-pinching is the observed breakup mechanism<sup>47</sup>. More recently, we studied the breakup of a drop of squalane in silicone oil in the presence of a poly-isobutylene succinimide surfactant (OLOA 11000). It was observed that the addition of the surfactant changes the breakup mode of the squalane drop from tipstreaming to end-pinching<sup>40</sup>. While the surfactants used in both the studies were soluble<sup>34,47</sup>, numerical studies for deformation of surfactant-laden interfaces under electric fields are restricted to insoluble surfactants  $^{37-40,42}$ . This is a good first approximation for predicting surfactant effects due to electrohydrodynamics, given the already complex coupling of several phenomena occuring in the process. In fact, accounting for Marangoni stresses due to nonuniform distribution of an insoluble surfactant, Lanauze, Sengupta and co-workers were able to qualitatively explain the change in experimentally observed breakup mode from tipstreaming to end-pinching $^{40}$ . An inherent assumption in all these computations is that the electric field does not change the adsorption isotherm. However there are no experiments to justify this assumption.

The solubility of the surfactant needs to be considered in order to accurately determine the time for breakup. This is exemplified in the work of Lanauze, Sengupta and co-workers<sup>40</sup>. Figure 1.2 shows the transient deformation of a squalane drop containing 0.12 wt% OLOA surfactant in silicone oil obtained from experiments and computations, and is reproduced from that work (Figure 8(a) of that paper). They show that including Marangoni stresses in the computations is required to predict the correct breakup mode, however modeling the surfactant as insoluble gives an incorrect estimate of breakup time. The breakup time predicted by the computations is nearly twice longer than the actual breakup time observed in experiments. In applications, an operator not only needs to know the size of the formed drops, but also the time at which breakup will occur. Hence, modeling soluble surfactants under electric fields is an essential problem. However, more fundamental questions regarding the transport of soluble surfactants need to be answered before this can be attempted. <u>The transport of surfactants under an external electric field has not been studied before. It needs to be determined if the surfactant transport is influenced by an electric field. In chapters 5 and 6, we quantify surfactant transport to oil-water interfaces under an external electric field.</u>



Figure 1.2: Experiment and computations illustrating the transient deformation of a squalane drop containing 0.12 wt% OLOA surfactant. Here the drop is suspended in silicone oil and the applied field strength is 2.5 kV/cm.

### **1.2** Structure of thesis

In this thesis, we address the gaps identified above, as indicated by the underlined text. In chapter 2, we quantify the deformation of a weakly conducting, 'leaky dielectric,' drop in a density matched, immiscible, weakly conducting medium under a uniform DC electric field. We exclusively consider prolate drops, for which the drop elongates in the direction of applied field. Furthermore, we assume the drop and medium to have equal viscosities. Using axisymmetric boundary integral computations, we delineate drop deformation and breakup regimes in the  $Ca_E - Re_E$  parameter space, where  $Ca_E$  is the electric capillary number (ratio of the electric to capillary stresses); and  $Re_E$ is the electric Reynolds number (ratio of charge relaxation to flow time scales), which characterizes the strength of surface charge convection along the interface. For so-called 'prolate A' drops, where the surface charge is convected towards the 'poles' of the drop, we demonstrate that increasing  $Re_E$  reduces the critical capillary number for breakup. Moreover, surface charge convection is the cause of an abrupt transition in the breakup mode of a drop from end-pinching, where the drop elongates and develops bulbs at its ends that eventually detach, to a breakup mode characterized by the formation of conical ends. On the contrary, the deformation of 'prolate B' drops, where the surface charge is convected away from the poles, is essentially unaffected by the magnitude of  $Re_E$ . This chapter has been published in the Journal of Fluid Mechanics as an article<sup>67</sup>.

In chapter 3 (submitted to *Physical Review Fluids*), we shed light on the response of drops in applications like electrocoalescence and electro-emulsification, where factors like interactions with surrounding drops or disturbances in operating conditions can produce a random field around a 'test' drop, even when the applied macroscopic field is uniform. We quantify the transient defor-
mation and breakup of a conducting drop suspended in a dielectric medium and subjected to a fluctuating electric field. Specifically, the magnitude of the field fluctuates randomly in time, while its orientation is fixed. Hence, the deformation of the drop is axisymmetric about the direction of the field. The temporal fluctuations are described by a stationary Markovian Gaussian process, characterized by a mean, variance and correlation time. We first develop a small deformation theory and predict that the fluctuations produce a larger deformation than under a constant electric field of strength equal to the mean of the fluctuating electric field. Next, we utilize boundary integral computations to quantify the deformation and breakup of drops beyond the small deformation regime. When the mean of the fluctuating field is greater than the critical field for breakup under a steady field, we find that the average time taken to undergo breakup is less than that under an equivalent steady field. More interestingly, a certain fraction of drops are observed to undergo breakup even when the mean field is less than the steady critical field. The fraction of drops undergoing breakup and the range of mean electric field below the steady critical where breakup is observed depends on the strength of fluctuations of the electric field. An operating map is presented for the percentage of drops undergoing breakup as a function of the dimensionless mean field for different strength of field fluctuations.

In chapter 4, we analyze the role of surfactant solubility and transport in the rheology of emulsions. We calculate the effective viscosity of a dilute emulsion of spherical drops containing a soluble surfactant under a linear creeping flow. It is assumed that convection of surfactant is small relative to diffusion, and thus the Peclet number, Pe, is small. We calculate the effective viscosity of the emulsion to  $\mathcal{O}(Pe\phi\mu_o)$ , where  $\phi$  is the small volume fraction of the dispersed drops, and  $\mu_o$  is the viscosity of the surfactant-free suspending fluid. This  $\mathcal{O}(Pe\phi\mu_o)$  contribution is a sensitive function of the bulk and interfacial surfactant transport. Specifically, soluble surfactants diffuse from the bulk to the interface, and then adsorb to the interface. The ratio of the time scale for bulk diffusion to the time scale for adsorption to the interface is quantified by a Damkohler number, Da. The adsorption of surfactant to the interface may cause a significant decrease in the bulk concentration, which is known as depletion. The impact of depletion is characterized by two parameters: h, which is a dimensionless depletion depth; and k, which is the ratio of the desorption time scale to the adsorption time scale. We analytically determine how the  $\mathcal{O}(Pe\phi\mu_o)$  contribution to the effective viscosity depends on h, k and Da. Surprisingly, for certain regimes in the h-k-Da parameter space, we predict the effective viscosity of the emulsion to be greater than Einstein's result for the viscosity of a suspension of rigid spheres. Large Marangoni stresses driven by convective transport of soluble surfactant molecules are responsible for this result. This chapter has been published in *Rheologica Acta* as an article<sup>68</sup>.

In chapter 5, we establish that electric fields can influence the transport of oil-soluble surfactants to oil-water interfaces. We use a custom-built electrified capillary microtensiometer platform to quantify the transport dynamics of oil-soluble surfactants to oil-water interfaces. Dynamic interfacial tension measurements reveal that the transport of a poly-isobutylene succinimide surfactant (OLOA 11000) is enhanced to an Isopar-water interface under a D.C. electric field. On the contrary, the transport of a triblock copolymer surfactant (Pluronic L64) to a silicone oil-water interface is unaffected by the electric field. The electrical conductivity measurements of the oils as a function of added surfactant show that the OLOA surfactant forms charge carriers in Isopar, while no such charged species are formed by the Pluronic surfactant in silicone oil. Analyzing the time scales of diffusion to the interface and transport by electrophoresis under an electric field, we conclude that electrophoresis of charge carriers is responsible for the field-enhanced transport of OLOA to the Isopar-water interface. Notably, this enhancement can be precisely tuned by altering the field strength and temporal scheduling. For the first time, we demonstrate electric fields as a new parameter to manipulate surfactant transport to microscale fluid-fluid interfaces. This chapter has been published as an article in *Physical Review*  $E^{69}$ .

In chapter 6 (submitted to the *Journal of Colloid and Interface Science*). we extend the observations in chapter 5, and probe other surfactant systems that form charged aggregates in the oil phase. The tendency of surfactant aggregates to acquire charge depends on surfactant architecture, and the solvent in which the surfactant is dispersed. In this chapter, we disperse two surfactants with different architecture in Isopar-M, and using the electrified microtensiometer platform, quantify the transport of surfactants to the oilwater interface under a constant electric field. Electrical conductivity of the oil with increasing surfactant concentration was measured to determine the presence of charge carriers. The charging mechanism of the oil phase, and the transport under an electric field was different for the two surfactants. At low concentrations where the electrical conductivity of the two surfactants are indistinguishable, dynamic interfacial tension measurements under electric fields can ascertain the presence of charge carriers in the oil phase. Experiments on the transport of ionic surfactants in the aqueous phase did not show an electric field-dependent effect because the electric field in the aqueous phase, which scales as the ratio of conductivity of the oil to aqueous phase, is essentially zero. This further confirms that the field-enhanced transport of oil-phase surfactants is due to electrophotresis of charge carriers. Moreover, the equilibrium interfacial tension was not found to change under an electric field, suggesting the adsorption isotherm is not a function of the field strength. We demonstrate that dynamic interfacial tension measurements under electric fields is a sensitive technique to detect the presence of charge carriers in a nonpolar fluid.

Finally, chapter 7 summarizes the major contributions and findings of this thesis, and provides directions for future research to further develop electric fields as a tool of manipulate fluid-fluid interfaces.

The chapters are written to be self-contained, hence there is some amount of repetition in the introductory sections for some of the chapters.

The work presented in this thesis will bridge the gap between the fields of electrohydrodynamics and surfactant transport to interfaces. This presents the first quantification of surfactant transport under electric fields. The results will direct further work in electrohydrodynamics of surfactant-laden interfaces. Electric fields have been demonstrated to have an instantaneous and selective control on surfactant transport, and can be tuned to engineer liquid-liquid interfaces. The electrified microtensiometer platform developed here can be used to determine how surfactant properties can be changed to elicit a desired field-induced response and inform the molecular design of surfactants. The knowledge of surfactant transport under electric fields obtained from the experiments can be fed as transport and interface parameters into the computational tools developed to model electrohydrodynamics of interfaces with soluble surfactants.

## Chapter 2

# The role of surface charge convection in the electrohydrodynamics and breakup of prolate drops

## 2.1 Introduction

When an electric field is applied across a drop of fluid suspended in another fluid, a jump in electric stress is generated at the interface due to a mismatch in the electrical properties between the fluids. For perfectly conducting or perfectly dielectric drops, suspended in a perfectly dielectric fluid, the resultant electric traction solely acts normal to the interface, and is balanced by capillary traction due to surface tension. The electric traction is nonuniform along the interface, and consequently, the drop becomes elongated along the direction of the applied field into a *prolate* shape<sup>17–20,22,23</sup>. For such systems, there is no fluid motion at steady state, and this phenomenon is called *electrohydrostatics*.

The problem becomes more complicated if both the fluids are weakly conducting, or *leaky dielectrics*. Drops of such fluids can also deform perpendicular to the applied field into *oblate* shapes<sup>21</sup>. This was explained by Taylor in his '*leaky dielectric model*'<sup>24</sup>. The conductivity of such fluids is typically

less than  $10^{-9}$  S/m, which is, for example, very small compared to distilled water, that has a conductivity of around  $10^{-4}$  S/m. Since the conductivity is not zero, however, as is the case with perfect dielectrics, charge carriers can be transported from the bulk fluids to the interface under an electric field. The characteristic time for a charge to reach the interface is given by the charge relaxation time scale,  $t_{e(i,o)} = \varepsilon_{i,o}/\sigma_{i,o}$ , where  $\varepsilon$  is the permittivity and  $\sigma$  is the conductivity, and the subscripts 'i' and 'o' refer to properties of the drop and the medium, respectively. The action of the imposed field on the accumulated charge at the interface generates a component of the electric stress tangential to the interface, in addition to a normal component. This requires a tangential viscous stress to balance it, which is why a flow is generated. The flow is sustained even if the system reaches a steady state, and this phenomenon is therefore referred to as *electrohydrodynamics*<sup>23,24,70</sup>. A leaky dielectric drop can deform into either a prolate or an oblate shape, depending on the properties of the drop and the medium.

Taylor's small deformation theory predicts the steady state deformation of the drop to be

$$\mathcal{D}_T = \frac{9}{16(2R+1)^2} \Big[ \frac{3R(3M+2)(1-RS)}{5(M+1)} + R^2(1-2S) + 1 \Big] Ca_E, \quad (2.1)$$

where,  $R = \sigma_o/\sigma_i$  is the ratio of conductivity of the medium to the drop,  $S = \varepsilon_i/\varepsilon_o$  is the ratio of the permittivity of the drop to the medium; and  $M = \mu_i/\mu_o$  is the ratio of viscosity of the drop to the medium, with  $\mu$  denoting the viscosity. Note that in his original paper, Taylor had used an inverse definition of M, S and R. The steady state deformation is defined as  $\mathcal{D}_T = (L-B)/(L+B)$ , where L and B denote the semiaxes along and perpendicular to the applied field, respectively (Figure 1). The electric capillary number,  $Ca_E = \varepsilon_o a_0 E_{\infty}^{*^2}/\gamma$  is the ratio of electric stress ( $\varepsilon_o E_{\infty}^{*^2}$ ) to capillary stress  $(\gamma/a_0)$ , where  $a_0$  is the radius of the undeformed drop, and  $\gamma$  is the interfacial



Figure 2.1: Schematic of electric field induced prolate deformation of a leaky dielectric drop. The axis of rotational symmetry,  $\varphi$ , is along the direction of the applied field. The drop of viscosity  $\mu_i$ , permittivity  $\varepsilon_i$  and conductivity  $\sigma_i$  is suspended in a fluid of viscosity  $\mu_o$ , permittivity  $\varepsilon_o$  and conductivity  $\sigma_o$ . Here, the charge relaxation time scale of the drop,  $t_{e,i} = \varepsilon_i/\sigma_i$  is smaller than the charge relaxation time scale of the medium,  $t_{e,o} = \varepsilon_o/\sigma_o$ . Consequently, the charging of the interface is controlled by the drop, and the induced flow is directed from the equator ( $\theta = \pi/2, 3\pi/2$ ) to the poles ( $\theta = 0, \pi$ ). The curved arrows denote the direction of fluid flow.

tension. The capillary number is calculated based on the medium properties. The capillary number can also be defined as the ratio of the capillary time scale,  $t_{c,o} = \mu_o a_0/\gamma$ , which represents the time taken by the capillary force to restore the drop to its undeformed state, to the flow time scale,  $t_{f,o} = a_0/U$ , where the velocity scale is obtained by balancing shear and electric stresses, and is given by  $U = \varepsilon_o \mu_o E_{\infty}^{*^2}/a_0$ . Taylor's theory is valid for small values of the capillary number,  $Ca_E \ll 1$ , and predicts that the drop deforms into a spheroidal shape: prolate if  $\mathcal{D}_T > 0$ , and oblate if  $\mathcal{D}_T < 0$ .

Taylor's small deformation theory qualitatively explains oblate and prolate deformations based on the properties of the fluids. It predicts accurate values for the deformation at small  $Ca_E$ , however a quantitative match at larger  $Ca_E$  with experiments is poor, with the theory underestimating the measured deformations $^{25,27,50}$ . The inclusion of higher order terms to Taylor's model<sup>28</sup> does not resolve this discrepancy. Droplet deformation at larger  $Ca_E$ has received attention in numerical studies to determine the steady state deformation, as well as breakup of drops<sup>26,29,30,32–34,71–74</sup>. At larger deformations, the drop shape may substantially deviate from a spheroid  $^{26,32,34}$ . Sherwood  $^{26}$ was the first to computationally study the steady shapes and breakup modes of leaky dielectric prolate drops under creeping flow conditions (i.e., the flow Reynolds numbers,  $Re_{i,o} = \rho_{i,o}a_0 U/\mu_{i,o}$  was assumed to be zero) using the boundary integral method. In his study, the viscosity of the drop was considered to be equal to that of the medium, and the effect of R and S on the final state of the drop was analyzed. Sherwood identified two modes of breakup: end-pinching, where a drop elongates into a cylindrical thread, and develops two or more lobes which eventually detach from the thread; and breakup by pointed ends. He concluded that pointed ends are observed when the permittivity of the drop is high compared to that of the medium, and end-pinching is observed when the conductivity of the drop is higher than that of the medium. Lac and Homsy performed boundary integral computations to investigate the behavior of a leaky dielectric drop in a wider parameter space, by varying M, S and  $R^{32}$ . Both prolate and oblate deformations were considered in their study, which identified various steady and unsteady shapes, some characterized by multiple lobes. The effect of fluid inertia was probed by some studies, where finite values of  $Re_{i,o}$  were considered<sup>29,30,75</sup>. These studies show that for cases with realistic values of fluid properties and applied fields, where the flow Reynolds number,  $Re \sim \mathcal{O}(1)$ , inertia does not play a significant role in leaky dielectric prolate drop systems.

Although the studies by Sherwood<sup>26</sup>, and Lac and Homsy<sup>32</sup> dealt with leaky dielectric drops, they neglected the effects of surface charge convection, by effectively assuming that the interface is charged instantaneously, i.e., the charge relaxtation time  $(t_e)$  is much smaller than the flow  $(t_f)$  and capillary  $(t_c)$ times. This assumption simplifies the analysis by decoupling the electrostatic and fluid flow problems; however, in experiments the value of the charge relaxation time scale can be comparable to the flow and capillary time scales<sup>34</sup>. Moreover, including a non-zero  $t_e$  is important to predict electrohydrodynamic tipstreaming of films and drops of leaky dielectric fluids. The size of the drops that are shed as a result of tipstreaming, and the charge carried by the daughter drops depend on  $t_e^{33,73}$ . Surface charge convection is quantified by the electric Reynolds number,  $Re_{E(i,o)} = t_{e(i,o)}/t_{f(i,o)} = \varepsilon_{i,o}^2 E_{\infty}^{*^2}/\mu_{i,o}\sigma_{i,o}^{70}$ . Experiments have shown that charge convection affects the onset of electrorotation for oblate drops, and possibly contributes to the hysteresis observed in the transition from axisymmetric to asymmetric shapes of the  $drops^{50}$ . Computations have demonstrated that surface charge convection leads to the development of 'charge shocks' near the equator of oblate drops, where steep gradients develop in the surface charge density profile<sup>34,74</sup>. The effect of surface charge convection was also incorporated in some other works<sup>30,72,76</sup>. These studies concluded that surface charge convection reduces the steady deformation of oblate drops; enhances the steady deformation of prolate drops; and that accounting for surface charge convection is important to characterize the transient dynamics of the drop.

In this chapter, we demonstrate that surface charge convection plays a more profound role for prolate drops than just enhancing the steady state deformation, as has been previously reported<sup>30,72,76</sup>. Prolate drops can support flows that are directed from the equator to the poles of the drop (Figure 2.1), as well as flows from the poles to the equator. Through boundary integral computations, we show that in the former case, surface charge convection can lead to an abrupt transition in breakup mode from end-pinching to breakup by the formation of conical ends. We mainly focus on drops having the same viscosity as the medium (M = 1) and study the breakup modes of the drops as the electric Reynolds number is increased from zero to finite values.

## 2.2 Problem formulation

Consider an initially uncharged, weakly conducting drop of initial radius  $a_0$ suspended in a weakly conducting medium (Figure 2.1). The drop and medium have the same density and same viscosity. A uniform DC field,  $E^*_{\infty}$ , is applied, which induces flow in both the fluids. Prolate drops can experience flows directed either from the equator  $(\theta = \pi/2, 3\pi/2)$  to the poles  $(\theta = 0, \pi)$  of the drop, or vice versa. The direction of the fluid flow depends on the charge relaxation time scales of the drop and the medium. If  $t_{e,i} < t_{e,o}$ , the flow is from the equator to the poles (Prolate A, or ' $PR_A$ ,' drops), and if  $t_{e,i} > t_{e,o}$ , the flow runs from the poles to the equator ( $PR_B$  drops). In this study, we will predict the drops to deform into non-spheroidal shapes, with multiple lobes. For such shapes, it is difficult to choose a semi-minor axis to quantify the deformation of the drop, per Taylor's definition. Hence, the deformation is defined as  $\mathcal{D}_{asp} = L/a_0$ , where L denotes the half length of the drop, and is equivalent to the semi axis along the electric field used in Taylor's definition. The effect of charge convection, characterized by  $Re_E$ , on the breakup mode of the drop is quantified.

The electrohydrodynamic problem requires in principal the calculation of the electric field and the fluid flow inside and outside the drop, and the shape of the drop with time. We employ the boundary integral method to solve this problem. This requires the solution of the field and flow at the interface only, thereby reducing the dimensionality of the problem and hence the computational cost<sup>77–79</sup>. Coupling between the electric field and fluid flow occurs at the interface due to the convection of charge by the electrohyrdodynamic flow.



Figure 2.2: Schematic showing the discretization of the undeformed drop, the unit tangential (s) and normal (n) vectors, the continuous tangential coordinate (s), and a fixed source point on the interface (x).

This is accounted for through the interfacial charge conservation equation. We now present the governing equations. Henceforth, a superscript '\*' denotes a dimensional variable, and a lack of the superscript denotes a physical parameter, scale, dimensionless group, or the dimensionless version of a dimensional variable.

#### 2.2.1 Electric field

The first step is to solve for the electric field and electric stress at the interface. The electric field is irrotational, and since the drop is electrically neutral, Gauss's law for electrostatics reduces to the Laplace equation for the inner and outer electrostatic potentials, giving  $\nabla^{*2}\phi_{i,o}^* = 0$ , with the electric fields given by  $E_{i,o}^* = -\nabla^*\phi_{i,o}^* \overset{32,34,80,81}{\rightarrow}$ . The electric field in the medium satisfies the condition  $E_o^* = -\nabla^*\phi_o^* \rightarrow E_\infty^*$  at large distances from the drop. In addition, the field also satisfies the interface conditions of continuity in the tangential component of the electric field, and a jump in the normal electric displacement due to the accumulation of interfacial charge<sup>32,34,80</sup>, namely,

$$E_{t,o}^* = E_{t,i}^*, (2.2)$$

and

$$\varepsilon_o E_{n,o}^* - \varepsilon_i E_{n,i}^* = q^*, \qquad (2.3)$$

where  $E_{t(i,o)}^* = \mathbf{E}_{i,o}^* \cdot \mathbf{s}$  is the tangential component of the inner and outer electric fields, respectively, and  $\mathbf{s}$  is a unit tangent vector, positive in the counterclockwise direction. The normal component of the electric field is given by  $E_{n(i,o)}^* = \mathbf{E}_{i,o}^* \cdot \mathbf{n}$ , where  $\mathbf{n}$  is a unit normal vector, positive in the outward direction (Figure 2.2), and  $q^*$  is the interfacial charge density.

We first non-dimensionalize the problem. Distance is non-dimensionalized with the radius of the undeformed drop,  $a_0$ . The magnitude of the applied electric field,  $E_{\infty}^*$ , is used to normalize the electric fields. Surface charge density is rendered dimensionless using  $\varepsilon_o E_{\infty}^*$ , and time is normalized by the capillary time,  $t_c = \mu_o a_0 / \gamma$ . The fluid flow is driven by the electric stress acting at the interface. Thus, the velocity scale is obtained by balancing the electrical stress with the viscous shear stress, giving  $U = \varepsilon_o E_{\infty}^{*^2} a_0 / \mu_o$ . Using these scalings, the Laplace equation is recast into a non-dimensional integral equation<sup>32,34,81</sup>

$$\boldsymbol{E}_{\infty} \cdot \boldsymbol{n}(\boldsymbol{x}) - \frac{1}{4\pi} \oint_{A} \frac{\boldsymbol{r} \cdot \boldsymbol{n}(\boldsymbol{x})}{r^{3}} (E_{n,o}(\boldsymbol{y}) - E_{n,i}(\boldsymbol{y})) dA(\boldsymbol{y}) = \frac{1}{2} [E_{n,o}(\boldsymbol{x}) + E_{n,i}(\boldsymbol{x})],$$
(2.4)

where  $\mathbf{r} = \mathbf{y} - \mathbf{x}$  is the distance between an observer point  $\mathbf{y}$  that can move along the interface, and a fixed source point  $\mathbf{x}$  on the interface. The integral is taken over the surface area A of the drop. Equation (2.4) has two unknowns  $E_{n,o}$  and  $E_{n,i}$ . Using the dimensionless form of (2.3),  $E_{n,i} = (E_{n,o} - q)/S$ , to substitute for  $E_{n,i}$ , (2.4) can be written as<sup>34</sup>

$$\frac{S-1}{4\pi S} \oint_{A} \frac{\boldsymbol{r} \cdot \boldsymbol{n}(\boldsymbol{x})}{r^{3}} E_{n,o}(\boldsymbol{y}) dA(\boldsymbol{y}) + \frac{S+1}{2S} E_{n,o}(\boldsymbol{x}) = \mathbf{E}_{\infty} \cdot \boldsymbol{n}(\boldsymbol{x}) - \frac{1}{4\pi S} \oint_{A} q(\boldsymbol{y}) dA(\boldsymbol{y}) + \frac{1}{2S} q(\boldsymbol{x}).$$
(2.5)

To calculate the normal electric field, a knowledge of the surface charge density is required. The interface is initially uncharged, and hence  $E_{n,o}$  and subsequently  $E_{n,i}$  can be computed at t = 0.

After calculating the normal electric fields inside and outside the drop, the tangential fields are obtained by an integral transformation of the Laplace equation in terms of the electrostatic potential,  $\phi_o^{34,82}$ ,

$$\phi_o(\boldsymbol{x}) = \phi_\infty(\boldsymbol{x}) + \oint_A \frac{1}{4\pi r} (E_{n,o}(\boldsymbol{y}) - E_{n,i}(\boldsymbol{y})) dA(\boldsymbol{y}).$$
(2.6)

The tangential field is obtained using  $E_{t,o} = -\partial \phi_o / \partial s$  and (2.2). Here, s is the tangential coordinate measured from  $\theta = 0$  (Figure 2.2). From the normal and tangential components of the electric field inside and outside the drop, the jump in electric traction at the interface from inside the drop to outside is evaluated as

$$[\boldsymbol{\tau}_{\boldsymbol{E}} \cdot \boldsymbol{n}] = \frac{1}{2} [(E_{n,o}^2 - SE_{n,i}^2) + (S-1)E_{t,o}^2]\boldsymbol{n} + E_{t,o}(E_{n,o} - SE_{n,i})\boldsymbol{t} = \Delta p_E \boldsymbol{n} + qE_{t,o}\boldsymbol{t},$$
(2.7)

where  $\tau_{E(i,o)} = E_{i,o}E_{i,o} - E_{i,o}^2 I/2$  is the dimensionless form of the Maxwell stress tensor, and  $\varepsilon_o E_{\infty}^{*^2}$  is the scale used to non-dimensionalize it. The jump in normal component of the electric traction is denoted by  $\Delta p_E$ , and is called the electric pressure, and the tangential component of the jump in electric traction, which is responsible for maintaining a flow, is  $qE_{t,o}$ .

#### 2.2.2 Fluid flow

The flow of fluid is sustained by the tangential component of the electrical stress. In this study, we assume creeping flow, Re = 0. Although in experiments  $Re \sim \mathcal{O}(1)^{34}$ , computations have shown that including fluid inertia at  $Re \sim \mathcal{O}(1)$  makes little difference in the steady state deformations from the results obtained using  $Re = 0^{30,75}$ . Thus, the flow satisfies the equation of continuity, along with Stokes equations, which when cast as integral equations in a dimenisonless form becomes<sup>83</sup>

$$\boldsymbol{u}_{\boldsymbol{o}}(\boldsymbol{x}) = -\frac{1}{8\pi} \oint_{A} \Delta \boldsymbol{f}(\boldsymbol{y}) \cdot \boldsymbol{J}(\boldsymbol{y}, \boldsymbol{x}) dA(\boldsymbol{y}), \qquad (2.8)$$

where J denotes the free-space Green's function for velocity, and

$$\Delta \boldsymbol{f} = \frac{2\kappa_m \boldsymbol{n}}{Ca_E} - [\boldsymbol{\tau}_E \cdot \boldsymbol{n}] \tag{2.9}$$

is the jump in hydrodynamic traction at the interface, where  $\kappa_m$  is the mean curvature defined as<sup>30</sup>

$$\kappa_m \boldsymbol{n} = \frac{1}{2} \Big[ \frac{d\boldsymbol{s}}{ds} + \frac{\boldsymbol{n}}{r} \frac{dz}{ds} \Big], \qquad (2.10)$$

and  $Ca_E = \varepsilon_o E_{\infty}^{*^2} a_0 / \gamma$  is the electric capillary number based on medium properties.

#### 2.2.3 Interfacial charge conservation

After obtaining the interfacial velocity, the surface charge density is updated. This is performed using the interfacial charge conservation equation<sup>23,70</sup>, which reads in dimensionless form,

$$Sa\frac{\partial q}{\partial t} + Re_E \,\boldsymbol{\nabla_s} \cdot (\boldsymbol{u_o}q) = \frac{E_{n,i}}{R} - E_{n,o}, \qquad (2.11)$$

where  $Re_E = \varepsilon_o^2 E_{\infty}^{*^2}/\mu_o \sigma_o$  is the electric Reynolds number based on medium properties, and  $Sa = Re_E/Ca_E$  is the Saville number, which is the ratio of the charge relaxation time scale to the capillary time scale. The first term on the left-hand side of (2.11) represents the transient charging of the interface, i.e., the charge relaxation. The second term accounts for surface charge convection, and changes in the surface charge density due to dilation of the interface. This term couples the electric field and fluid flow equations due to the presence of  $u_o$ . The terms on the right-hand side account for the Ohmic conduction of charges from the bulk to the interface and vice versa. Finally, the interface is updated using the dimensionless kinematic condition

$$\frac{d\boldsymbol{x}}{dt} = Ca_E(\boldsymbol{u_o} \cdot \boldsymbol{n})\boldsymbol{n}.$$
(2.12)

#### 2.2.4 Numerical scheme

Equations (2.5), (2.6) are (2.8) are solved sequentially via the boundary element method. The details of the numerical method have been provided in

earlier<sup>34</sup>, and will therefore only be briefly discussed here. The field and flow are assumed to be axisymmetric, allowing an analytical integration over the azimuth, which reduces the surface integrals to line integrals over the contour of the drop. The top half of the drop is partitioned into N elements. This creates N+1 nodes, which are called source points, and whose coordinates are denoted by  $\boldsymbol{x}$ . All functions are interpolated as cubic splines with respect to s. The integral over the entire contour is replaced by a sum of integrals over each element. Singular terms in the integrands are subtracted out, and then added back, following standard regularization techniques<sup>82</sup>. Gauss-Legendre quadrature is used to evaluate the integrals, and the points at which the integrand is evaluated are termed observer points, their coordinates being denoted by y. After evaluating the field and flow equations, the surface charge density (2.11) and the shape of the interface (2.12) are updated using the second order Runge-Kutta method, and the deformation of the drop at every time instant is calculated. The time step is chosen such that the volumetric flow rate across the interface, which should be identically zero to conserve mass, is at most  $\mathcal{O}(10^{-6})$  for the initial 20 iterations. This ensures that the computations remain stable for the selected time step, and any instability occurs due to the breakup of the drop. If the volumetric flow rate across the interface remains  $\mathcal{O}(10^{-6})$  or less, while the maximum value of the radial velocity keeps on decreasing, and reaches  $\mathcal{O}(10^{-4})$  or less, we conclude that the drop has attained a steady shape. If the volumetric flow rate slowly starts to increase, along with an increase in the maximum value of the radial velocity, we conclude that the drop shape is unsteady, and it will eventually break up. The boundary integral method cannot track the interface after the drop breaks, and in this case, the results are reported at a time instant very close to breakup, where the ratio of volumetric flow rate across the interface to the initial volumetric flow rate is  $\mathcal{O}(10^2)$ . For all our computations, the top half of the drop was divided into

150 elements, and the time step size was taken to be 0.05. These values were chosen after performing a convergence analysis, the results of which are given in Appendix A.

## 2.3 Flow in prolate drops

At  $Ca_E \ll 1$ , and neglecting surface charge convection,  $Re_E = 0$ , the electrohydrodynamic problem has been solved analytically for DC electric fields<sup>24</sup>. Depending on the ratios M, S and R, the drop can deform into prolate or oblate shapes, or even remain spherical. Oblate drops only support flows directed from the poles to the equator, whereas depending on the ratios, prolate drops can support flows directed from the equator to the poles ( $PR_A$  drops), as well as flows directed from the poles to the equator ( $PR_B$  drops). Figure 2.3 depicts various behaviors of the drop in the (R - S) space when M = 1. This figure has been previously shown by other researchers<sup>25,32,53</sup>; it is reproduced here to provide a context for our nonlinear computations.

When the charge relaxation time scale of the drop is smaller than that of the medium (RS < 1), the charging of the interface is controlled by the drop. The interface gets charged in a fashion depicted by the  $PR_A$  region of Figure 2.3. This results in an electric stress, whose tangential component acts from the equator to the poles, giving rise to fluid flow in that direction. Regardless of the value of M, prolate A behavior occurs when RS < 1, in the region below the dashed line. The locus of the solid line is<sup>25</sup>

$$RS = 1 + \frac{5(1+M)}{16+19M} \frac{(R-1)^2}{R},$$
(2.13)

and along this line the drop remains spherical. This line also demarcates regions of oblate deformation from regions of prolate deformation. In the



Figure 2.3: (R - S) parameter space diagram for M = 1. The solid line distinguishes regions showing prolate deformation from regions showing oblate deformation. Points along the solid line remain spherical under an applied electric field (at small  $Ca_E$ ). The dotted line separates drops showing prolate A  $(PR_A)$  behavior from drops showing prolate B  $(PR_B)$  behavior. The four symbols on the diagram represent the four systems considered in this study. The curved arrows around the drops show the direction of the induced flow in each of these regions. The electric field is applied from left to right, and is shown by straight arrows above the drops.

region between the solid line and the dashed line, i.e., where

$$1 < RS < 1 + \frac{5(1+M)}{16+19M} \frac{(R-1)^2}{R},$$
(2.14)

the drop deforms into prolate shapes, but the flow is directed from the poles to the equator. In this region RS > 1, and the charging of the interface is controlled by the medium. The interface charge distribution now gives rise to an electrical stress whose tangential component is directed from the poles to the equator, thus resulting in a similar flow direction. These are the results of small deformation theory, and give a first order estimate of the induced flow direction. The flow profile is expected to deviate when deformations are substantial and drop shapes become non-spheroidal. However, understanding the flow direction at small  $Ca_E$  is important to draw conclusions on the mode of breakup of prolate drops at larger  $Ca_E$ .

## 2.4 Results

The effect of surface charge convection on prolate A and prolate B drops is studied. We are interested in understanding how charge convection affects the breakup modes of these drops. The response of the drop depends on the ratios of viscosity, permittivity and conductivity, i.e., M, S and R; hence the computational parameter space is large. For the most part of this study, we assume M = 1, and choose different combinations of S and R, so as to cover different regions of the R - S parameter space. Here, we present results on two prolate A drops, and two prolate B drops; the R and S values for these drops are shown in Figure 2.3. Later, we provide a short discussion for cases where  $M \neq 1$ .

#### 2.4.1 Prolate A drops

The validity of our computational method with and without surface charge convection was established previously<sup>34</sup> by comparing the results of a system with (M, S, R) = (1, 0.5, 100) to the results of Feng<sup>30</sup>. Here, we first choose a system with (M, S, R) = (1, 1, 0.05), which corresponds to the filled circle symbol in Figure 2.3, and was studied by Sherwood<sup>26</sup> for the case  $Re_E = 0$ . This system deforms into a prolate shape and undergoes breakup at  $Ca_E =$ 0.28 for  $Re_E = 0$ . Computations were performed at this value of  $Ca_E$ , with  $Re_E$  increasing from zero to finite values. The results are shown in Figure 2.4.

At  $Re_E = 0$ , the drop initially stretches into a long cylinder. After sometime, bulbs form at the two ends, being connected by a thin thread of the



Figure 2.4: (a) Deformation,  $\mathcal{D}_{asp} = L/a_0$  versus electric Reynolds number,  $Re_E$  at  $Ca_E = 0.28$  and (M, S, R) = (1, 1, 0.05), showing the effect of surface charge convection on the breakup mode of a prolate A drop. The breakup mode changes from end-pinching to breakup by conical end formation over a narrow range of  $Re_E$ , as shown by the dashed region. The right panel shows the shape of the drop just before breakup at (b)  $Re_E = 0.08$ ; and (c) at  $Re_E = 0.18$ , with the dotted circle representing the shape of the undeformed drop. The arrow above the drops shows the direction of the applied electric field.

fluid. As time progresses, the connecting thread of fluid develops more bulbs, and forms a multi-lobed structure. Eventually, the bulbs pinch off from the thread. This mechanism of breakup is called end-pinching. The shape of the drop before breakup (Figure 2.4 (b)) is similar to the result of Sherwood<sup>26</sup> (Figure 8 of that paper). As  $Re_E$  is increased from zero, the mode of breakup remains the same, and the drop elongates slightly more before finally breaking. This trend continues until  $Re_E = 0.14$ . At  $Re_E = 0.15$ , the mode of breakup changes dramatically: the ends form conical tips, instead of bulbous ends. Increasing  $Re_E$  further does not change the mode of breakup, but the final deformation before breakup decreases. The only parameter that was changed in the computations was the electric Reynolds number, which quantifies the strength of charge convection. Thus, surface charge convection changes the breakup mode of this drop from end-pinching to the formation of conical ends at an  $Re_E$  between 0.14 and 0.15, and  $Ca_E = 0.28$ .

To understand why a transition in breakup mode takes place, consider the jump in the electrical stress at the poles ( $\theta = 0, \pi$ ) of the drop. Here, the tangential component of the electric field vanishes, and thus there is no jump in the tangential electric stress (2.7). Substituting the condition for the discontinuity in normal electric field at the interface, the electric pressure at the poles is given by

$$[\boldsymbol{\tau}_{\boldsymbol{E}} \cdot \boldsymbol{n}] = \Delta p_{\boldsymbol{E}} = \frac{q}{2} (q + 2SE_{n,i}), \qquad (2.15)$$

and it varies with the square of the surface charge density, q. The electric pressure drives the drop to breakup, while the capillary stress tends to restore its spherical shape. For the system being studied, the tangential velocity profile (Figure 2.5(a)) suggests that the flow occurs from the equator to the poles of the drop, and the radial velocity profile (Figure 2.5(b)) shows that the normal component of the velocity is very small at all points on the interface, except at the poles, where it rises sharply to values almost two orders of magnitude higher than at other points on the interface. Thus, the formation of pointed tips is accompanied by flow towards the tips of the drop.

We hypothesize that the transition in the breakup mode is caused by the accumulation of surface charge at the poles due to increased charge convection by the electrohydrodynamic flow at higher  $Re_E$ . The evolution of the surface charge density for a drop breaking via end-pinching ( $Re_E = 0.1$ ), and via the formation of conical ends ( $Re_E = 0.18, 1$  and 10) is shown in Figure 2.6 (a). When the field is turned on, the interface starts acquiring charge. Initially, the surface charge density evolves in a similar fashion for all the cases.



Figure 2.5: Interfacial velocity profile for a prolate A drop (M, S, R = 1, 1, 0.05) just before breakup. Here,  $Ca_E = 0.28$  and  $Re_E = 0.18$ . The drop breaks by the formation of pointed ends. (a) Dimensionless tangential velocity profile. The inset shows the drop shape before breakup, the dashed circle is the shape of the undeformed drop, and the dotted arrows above the drop show the direction of flow. (b) Dimensionless radial velocity profile.

At this early stage of charging, the drop behaves as a perfect dielectric<sup>34,84</sup>, because it takes a finite amount of time for the charges to reach the interface. The strength of the fluid flow during this stage is low, and hence the surface charge convection is negligible. Figure 2.6 (b) shows how the strength of the charge relaxation and surface charge convection (the two terms in the LHS of (2.11)) evolves with time. It follows that at early times, the strength of charge relaxation is at least three orders of magnitude higher than the strength of surface charge convection. During this time, charge relaxation is balanced by the discontinuity in the normal component of the electric field, and the surface charge density scales as  $q \sim \frac{t}{Sa} \left[\frac{1}{R} - 1\right]$ . The inset in Figure 2.6 (a) shows the early time charging at the poles for different electric Reynolds numbers. All the curves collapse when the dimensionless time is scaled by Sa. This initial period lasts till  $t/Sa \approx 0.1$ . After this, surface charge convection can no longer be neglected, and the early time scaling for the surface charge density no longer holds. The effect of charge convection is stronger for systems



Figure 2.6: (a) Evolution of surface charge density, and (b) strength of charge relaxation and surface charge convection at the poles ( $\theta = 0$ ). For (b), the solid curve represents a drop breaking via end-pinching ( $Re_E = 0.1$ ), and the dashed curve represents a drop breaking via the formation of conical ends ( $Re_E = 0.18$ ).



Figure 2.7: (a) Evolution of surface charge density, and (b) jump in the normal component of the electric and capillary stress at the pole ( $\theta = 0$ ). The solid curve represents a drop breaking via end-pinching ( $Re_E = 0.1$ ), and the dashed curve represents a drop breaking via the formation of conical ends ( $Re_E = 0.18$ ).

with a larger  $Re_E$  (Figure 2.6 (b)). Thus, drops with different values of the electric Reynolds number get charged differently after the initial period, and the distribution of surface charge density is affected by the strength of surface charge convection.

Figure 2.7 shows the evolution of surface charge density, and the jump in the normal electric and capillary stress at the poles of the drop, for the two modes of breakup (end-pinching for  $Re_E = 0.1$  and conical ends formation for  $Re_E = 0.18$ ). As time progresses, the surface charge density at the poles increases for both the cases. After surface charge convection becomes comparable to the other terms in (2.11), the charge carriers are convected more strongly to the poles for the system with a larger electric Reynolds number  $(Re_E = 0.18)$ . This system shows a monotonic increase in the surface charge density at the poles, and correspondingly, the electric pressure (Figure 2.7 (b)). To balance the electric pressure, the capillary stress also increases monotonically, and as a result, the curvature at the pole increases. Eventually the electric pressure dominates and the drop breaks via the formation of pointed ends. In contrast, for  $Re_E = 0.1$ , the surface charge density shows a maxima, implying that the charge carriers are convected back from the poles to points elsewhere on the interface. This suggests that there is a flow reversal occurring after a particular time. The ends of the drop develop bulbs sometime after this maxima occurs. The jump in the electric stress reaches a maximum value, after which it decreases, allowing the capillary stress to dominate at the poles. Here, the drop breaks at points on the interface where the charge carriers accumulate. Therefore, the breakup mode depends on whether the electric pressure or the capillary stress dominates at the poles.

The formation of conical tips and the evolution of the surface charge density and electric pressure at the tips resembles the onset of a conic cusping singularity, which has been observed for conducting and dielectric, inviscid fluids<sup>85,86</sup>; liquid metallic films in vacuum<sup>87</sup>; films of perfectly conducting fluids in an insulating gas<sup>33</sup>; and perfectly dielectric drops in oils<sup>88</sup>, under a uniform electric field. The characteristic feature of a conic cusping singularity is that the temporal evolution of physical quantities, like the surface charge density,



Figure 2.8: Evolution of the (a) curvature, and (b) surface charge density at the tips of drops showing conical ends. Here, (M, S, R) = (1, 1, 0.05), and  $Ca_E = 0.28$ .

fluid velocity, normal electric field, and the curvature, at the tips exhibit a runaway behavior. These parameters tend to become infinitely large in a finite time. Figure 2.8 shows the evolution of the curvature and the surface charge density at the tips for  $Re_E = \{0.18, 1\}$ . Both these quantities show a relatively slow growth until the onset of cusps, when they approach infintely large values over a relatively short span of time. Further, for systems showing a conic cusping singularity, the magnitude of the electric pressure at the tips becomes much larger than the capillary force, as is exhibited in Figure 2.7. Although previous computations predict leaky dielectric drops to break via the formation pointed tips, an analysis of the evolution of physical parameters and the curvature at the tip was not performed  $^{26,32}$ . Hence, it is unclear if the conical ends observed in those studies is conic cusping. Since the flow in the drops is directed from the equator to the poles, Sherwood<sup>26</sup> used the term "tipstreaming" to describe the breakup by pointed ends. However, tipstreaming necessitates the transition of cones to fine jets, followed by the disintegration of the jet into drops of size orders of magnitude smaller than

the parent drop<sup>33,71,73,89</sup>, and this transition was not observed in the studies of Sherwood<sup>26</sup>, and Lac and Homsy<sup>32</sup>. Figures 2.7 and 2.8 indicate that the system studied here undergoes a conic cusping singularity above a critical  $Re_E$ .

In Figure 2.9, we present the results for the final drop state across the  $Ca_E - Re_E$  parameter space, again for (M, S, R) = (1, 1, 0.05). From the expressions of  $Re_E$  and  $Ca_E$ , the magnitude of the applied electric field and the initial size of the drop are the two parameters that can be tuned to perform this parameter sweep experimentally. We find that as  $Ca_E$  is increased, the value of  $Re_E$  at which the transition in breakup mode occurs reduces. Drops breaking via end-pinching form a higher number of lobes before breaking as  $Ca_E$  increases beyond the critical capillary number. For this system, breakup via end-pinching occurs over a small region in the  $Ca_E - Re_E$  space; thus, the drop predominantly breaks via the formation of conical ends.

Next, we study another prolate A system with (M, S, R) = (1, 0.1, 0.1), which corresponds to the filled star symbol in Figure 2.3, and was first examined by Lac and Homsy<sup>32</sup> for  $Re_E = 0$  only. We again start with  $Re_E = 0$  and probe the effect of increasing the electric Reynolds number. The results are shown in Figure 2.10. The computations of Lac and Homsy<sup>32</sup> predict a critical capillary number of 0.342 for this system at  $Re_E = 0$ . We find that the drop breaks into two daughter drops at a critical capillary number of  $Ca_E = 0.35$ at  $Re_E = 0$ . The breakup mode observed by our computations is same as the one observed by Lac and Homsy<sup>32</sup> (Figure 5 of their paper). Further increasing the capillary number does not alter the breakup mode, but the number of lobes before breakup increases. This is due to the fact that the destabilizing force is larger at higher capillary numbers. Thus, the drop can get elongated to a larger extent, and be more prone to capillary instability. Similar to the system depicted in Figure 2.9, this system has a transition in breakup mode from end-pinching to conic cusping beyond a certain  $Re_E$ ; and shows breakup



Figure 2.9: Final state of the drop in the  $Ca_E - Re_E$  space for (M, S, R) = (1, 1, 0.05). Three states are identified in this diagram: steady prolate shapes, breakup by end-pinching, and conic cusping. The shapes have been normalized by the half length of the drop at steady state or just before breakup. Thus, drops that deform more appear thinner in this diagram. Drops attaining steady states, or breaking via end-pinching deform more as  $Re_E$ ,  $Ca_E$ , or both increases. For drops exhibiting conic cusping, the deformation just before breakup decreases as  $Re_E$ ,  $Ca_E$ , or both increases.

via end-pinching over a larger region in the  $Ca_E - Re_E$  parameter space as compared to the system depicted in Figure 2.9. Surface charge convection also reduces the critical capillary number for breakup; the drop exhibits conic cusping at  $Ca_E = 0.32$  when  $Re_E = 5$ , which is lower than the critical capillary number,  $Ca_E = 0.35$ , predicted at  $Re_E = 0$ .

In summary, for  $PR_A$  drops, our computations suggest that surface charge convection abruptly changes the breakup mode from end-pinching to conic cusping, and also reduces the critical capillary number for breakup. This is a consequence of the transport of charges along the interface, which in these



Figure 2.10:  $Ca_E - Re_E$  parameter space plot for (M, S, R = 1, 0.1, 0.1). Three states are identified in this diagram: steady prolate shapes, breakup by endpinching, and conic cusping. Refer to Figure 2.9 for details of the drop shape illustration.

systems, takes place from the equator to the poles. Additionally, for both systems, increasing  $Re_E$  reduces the time at which breakup occurs.

#### 2.4.2 Prolate B drops

We now consider prolate B drops, where small deformation theory predicts the flow to be directed from the poles to the equator. The value of our calculations here is twofold. First, we demonstrate that surface charge convection has a minor effect on the deformation of prolate B drops, as compared to prolate A drops. This highlights the important point that surface charge convection does not always lead to a significant change in drop deformation. Second, our computed steady deformations for prolate B drops are shown to compare favorably against predictions from slender-body theories<sup>81,90</sup>, which helps to assess the accuracy of the latter. Prolate B drops can be studied in experiments by choosing a pair of fluids that have a large contrast in the dielectric constant and conductivity. For example, a drop of squalane doped with polyisobutylene succinimide surfactant (OLOA 11000) in a polystyrene (PS) solution, dissolved in dimethylformamide (DMF) should show a prolate B response when subjected to an electric field. A squalane drop doped with 30 pph OLOA is characterized by  $\mu_i = 0.03$  Pa s,  $\varepsilon_i \sim 2$ ,  $\sigma_i = 2.2 \times 10^{-10}$ S/m<sup>40</sup>, and for a 15 wt% PS solution in DMF,  $\mu_o = 0.035$  Pa s,  $\varepsilon_o = 30.2$ ,  $\sigma_o = 7.6 \times 10^{-9}$  S/m<sup>91</sup>; yielding M = 0.86, S = 0.07 and R = 35.

We first study a system with (M, S, R) = (1, 50, 0.04), which corresponds to the triangle symbol in Figure 2.3, and was examined by Lac and Homsy<sup>32</sup> (Figure 16 of that paper). They found the system to become unstable at a capillary number of 0.47 when  $Re_E = 0$ , and the drop developed pointed ends before breaking. Since the flow is from the poles to the equator, Lac and  $Homsy^{32}$  did not categorize this mode of breakup as tipstreaming. We find this system to become unstable at  $Ca_E = 0.46$  when  $Re_E = 0$ , and the poles develop pointed ends. The tangential velocity profile shows the appearance of stagnation points very close to the poles just before breakup (Figure 2.11 (a) inset). The interfacial flow is directed from the stagnation points to the equator, as well as to the poles. Thus, charges are convected to the poles of the drop. When surface charge convection is accounted for, at non-zero  $Re_E$ , the breakup mode does not change. Pointed ends are formed, there are stagnation points very close to the poles, and the flow profile suggests surface charge convection to the poles. The evolution of the curvature, surface charge density and stress jumps at the tips suggest the onset of conic cusping both at  $Re_E = 0$ , and at finite values of  $Re_E$  (Figure 2.11 (d), (e) and (f)). The critical capillary number for breakup reduces, and the stagnation points move farther away from the poles as  $Re_E$  increases. Similar to  $PR_A$  drops, the



Figure 2.11: Dimensionless interfacial velocity for a prolate B system (M, S, R = 1, 50, 0.04) just before breakup at  $Ca_E = 0.46$  for (a)  $Re_E = 0$ , (b)  $Re_E = 1$ , and (c)  $Re_E = 3$ . Evolution of (d) the curvature, and (e) surface charge density at the tip of the drop at  $Re_E = \{0, 1\}$ . (f) Evolution of the electric pressure and the jump in capillary stress at the tips for  $Re_E = 1$ . The insets in the velocity profiles show the shapes of the drop just before breakup, with the dashed circles representing the shape of the undeformed drop.

time at which the drops undergo breakup decreases as  $Re_E$  increases. At the highest values of  $Re_E$ , the flow occurs from the equator to the poles, similar to that for prolate A drops (Figure 2.11 (c)). A large value of  $Re_E$  implies that the charge relaxation time scale is slow compared to the flow time scale. The flow sets up much faster than charges arrive at the interface. The drop behaves as a perfect dielectric at initial times<sup>34,84</sup>, and the flow occurs from the equator to the poles. The flow direction reverses as the interface acquires charge. If however, the charge relaxation time scale is much slower than the flow time scale, as is the case at large  $Re_E$ , the inner fluid may transport sufficient charge to the poles of the drop, so as to increase the electric pressure and cause conic cusping before the flow can reverse. Thus, the flow direction will be from the equator to the poles in this case.

We now consider a second  $PR_B$  drop with M = 1, S = 0.03 and R =50, shown by the square symbol in Figure 2.3. This system is most closely resembled by a drop of squalane doped with 30 pph OLOA, suspended in a 15 wt% PS solution in DMF. Here, the drop does not break even at the largest capillary numbers tested. The steady prolate shape of the drop is characterized by pointed ends, as shown in Figure 2.12. In this case, surface charge convection increases the final steady deformation of the drop, but it does not induce breakup. The strength of the induced flow is very weak, as seen in the figure. The flow is directed from the poles to the equator, and there are no stagnation points observed. At very high values of  $Ca_E$ , the drop assumes long, stable, slender shapes with pointed ends. The evolution of the surface charge density at the poles (Figure 2.12 (c)) shows that it does not diverge like the drops exhibiting conic cusping, but instead attains a steady value, implying that the conical tips observed for this drop are stable. Slender body theories for perfect dielectric and leaky dielectric drops in a uniform electric field predict stable drop shapes with conical ends<sup>81,90</sup>. These theories predict



Figure 2.12: Deformation of a  $PR_B$  drop, with (S, R) = (0.03, 50). (a) Deformation versus electric capillary number at  $Re_E = 0$  (shown by  $\circ$ ),  $Re_E = 1$  (shown by  $\times$ ) and  $Re_E = 10$  (shown by +). The top insets show the steady shape of the drop, and the dashed circle represents the undeformed drop. (b) Dimensionless interfacial tangential velocity,  $u_{\theta}$  profile at steady state for  $Ca_E = 58$ ,  $Re_E = 10$ . The inset shows the drop shape at steady state, and the curved lines show the direction of the induced flow. The arrow above the drop shows the direction of the applied electric field. (c) Evolution of dimensionless surface charge density at the tip for  $Ca_E = 58$ ,  $Re_E = 10$ .

the slenderness of the drop, defined as the ratio of the equatorial radius of the deformed drop to the half length of the drop, a/L (see inset to Figure 2.13) to scale with the inverse 3/7-power of  $Ca_E$ , under large applied fields, i.e., for  $Ca_E \gg 1$ . Figure 2.13 shows the results of our computations at viscosity ratios  $M = \{0.1, 1\}$ , both with and without surface charge convection. All the three results closely obey the scaling  $a/L \sim Ca_E^{-0.4285}$  predicted by the slender body theories (shown by the black curve). Although the theories have been developed under the assumptions of  $Re_E = 0$  and  $M \ll \mathcal{O}(a/L)^2$ , it is interesting to note that the computations accounting for surface charge



Figure 2.13: Slenderness of the drop as a function of the electric capillary number for a system with (S, R) = (0.03, 50). The symbols correspond to the results of our computations. The black line shows the curve  $a/L \sim Ca_E^{-3/7}$ . The inset shows a deformed drop with pointed tips. The equatorial radius is a, and the half length of the drop is L.

convection and  $\mathcal{O}(1)$  values of the viscosity ratio seem to closely follow the predicted scaling.

In summary, our computations suggest that surface charge convection does not affect the breakup mode of  $PR_B$  drops. In these systems, its role is to increase the final steady deformation of drops. For drops which ultimately break into smaller drops, surface charge convection reduces the time at which the drop undergoes breakup. Drops which deform into long, stable shapes under strong electric fields closely follow slender body theories, which predict the slenderness to scale as  $Ca_E^{-3/7}$ .

### 2.5 Discussion

End-pinching and breakup by the formation of pointed ends have both been observed in experiments on drops in electric fields. For highly conducting drops  $(R < 10^{-4})$  suspended in oils, end-pinching has been reported to be the mode of breakup<sup>21,25,31</sup>. For example, a drop of deionized water in castor oil, with  $(M, S, R) = (1 \times 10^{-4}, 6.3, 1 \times 10^{-5})$  at  $Ca_E = 0.2$  and  $Re_E = 0.15^{21}$ ; and a deionized water drop in silicone oil, with  $(M, S, R) = (0.001, 28, 1 \times 10^{-6})$ at  $Ca_E = 0.22$  and  $Re_E = 32$ , break via end-pinching<sup>31</sup>. Breakup via the formation of pointed ends has been observed for soap films<sup>22</sup>; sessile water drops exposed to air<sup>92,93</sup>; sessile water drops suspended in oils<sup>22</sup>; leaky dielectric systems and polymer  $drops^{31}$ ; and sessile drops of dielectric liquids in  $air^{93}$ . In nearly all these studies, the formation of the pointed end, or the conic cusp is followed by the ejection of a very fine jet of fluid, which then disintegrates into drops, whose sizes are orders of magnitude less than the parent drop. While our computations predict the onset of the conic cusp, the transition from the cone to jet is not captured. The transition from cones to fine jets, or the process of "electrohydrodynamic tipstreaming" has been resolved computationally for films and drops of leaky dielectric fluids exposed to air<sup>33,73</sup>, and electrolytic drops suspended in oils<sup>88,89</sup>. These studies accounted for the surface convection of charges, as well as the transient fluid inertia, by taking finite values of the Ohnesorge number, Oh, which is the ratio of capillary to momentum diffusion time scales. The evolution of curvature for a leaky dielectric drop exhibiting tipstreaming shows a rapid growth over a very short span of time, akin to conic cusping, which corresponds to the formation of a sharp tip. This is followed by a period of slower growth and then a rapid decline in the curvature due to the transition of the cone into a  $jet^{33}$ . The sharpening of the tip is accompanied by a rapid acceleration of fluid towards the tips, suggesting that

accounting for transient fluid inertia, in addition to the convection of charges might be important to capture the cone to jet transition. Our computations account for the surface convection of charges, but not transient fluid inertia, which possibly explains why the evolution of a jet is not observed. There is a sharp transition in the breakup mode of the drop, from disintegration by the formation of lobes to breakup characterized by the formation of cusps at the ends. It will be interesting to understand the mechanism by which the cusps undergo breakup.

From the two  $PR_A$  drops we studied, it is clear that the critical values of  $Ca_E$  and  $Re_E$  at which the transition from end-pinching to conic cusping occurs, and the operating space over which each breakup mode is observed. depend on the system being studied, i.e., on the values of M, S and R. The system shown in Figure 2.9 is predicted to show breakup via the formation of pointed ends over most of the operating space. It is most closely resembled by system 'NN21', of a 0.16 cm radius castor oil drop in silicone oil, studied by Ha and Yang<sup>31</sup>. Their experimental system was reported to have (M, S, R) =(0.874, 1.37, 0.1), and the drop was observed to break with pointed ends at  $Ca_E = 1.23$  and  $Re_E = 35$ . For these parameters, our computations indeed predict the appearance of pointed ends. In order to move into the region of end-pinching for this system, we have to start with drops having  $a_0 \sim 10$  cm or higher. It is difficult to apply uniform fields to such large drops in practice; thus for viable drop sizes, this system will show the formation of pointed ends. A castor oil drop suspended in another silicone oil (system 'NN17'), characterized by (M, S, R) = (0.08, 1.37, 0.1) showed breakup via end-pinching at  $Ca_E = 1.1$ and  $Re_E = 4.3^{31}$ . Our computations indeed suggest that lowering  $Ca_E$  and  $Re_E$  will shift the breakup mode from pointed ends to end-pinching, provided M, S and R remain constant. Systems 'NN17' and 'NN21' have the same values of R and S, however, M differs by an order of magnitude. It is important



Figure 2.14: Effect of viscosity ratio on the deformation and breakup of a prolate A drop. For this system, (S, R) = (1, 0.05),  $Ca_E = 0.28$ , with (a)  $Re_E = 0.05$ , and (b)  $Re_E = 0.2$ .

to recall here that we consider a viscosity ratio M = 1 for most of this study. Thus, one expects our results to be relevant to system 'NN21' (M = 0.874). However, the relevance of our results to low viscosity ( $M \ll 1$ , e.g. system 'NN17') or high viscosity drops  $(M \gg 1)$  is questionable. The viscosity ratio is known to have a great influence on the deformation and breakup of drops in shear and extensional flows<sup>79</sup>. Figure 2.14 shows the result of changing the viscosity of the drop on the deformation and breakup of a prolate A drop. Our computations predict a more viscous drop to deform more before undergoing breakup, and the strength of the interfacial flow to reduce for a more viscous drop, both in agreement with the observations of Lac and Homsy<sup>32</sup>; however, the breakup mode remains unchanged. Thus, for a prolate A drop, there is a quantitative change in breakup, but the breakup mode remains the same when there is a moderate change in M. The deformation of a prolate B drop was found to be essentially unaffected by the viscosity ratio. For the system with (S, R) = (0.03, 50), the deformation changed by 0.5 % when M was varied over two decades. It is expected that the boundaries demarcationg regions of steady state, end-pinching and conic cusping in the  $Ca_E - Re_E$ parameter space will change when the viscosity ratio changes, but as Figure 2.14 suggests, a transition will be observed. A detailed study investigating the effect of viscosity ratio on the transition in breakup mode is left as future work.

Weakly conducting oils like castor oil, silicone oil, squalane and polymers like polystyrene and polyvinylidene fluoride dissolved in suitable solvents have been used to perform experiments on leaky dielectric systems<sup>21,25,27,31,91</sup>. For these systems, the conductivity and the dielectric constant can be changed to different extents without altering the viscosity by doping with carbon black particles<sup>94</sup>; and the conductivity can be independently changed at constant viscosity and dielectric constant by doping with surfactants<sup>95,96</sup>. Thus, different regions of the R-S parameter space (Figure 2.3) can be accessed with leaky dielectric fluids. However, observing the predicted transition in breakup modes in the same system might be difficult in experiments, because experimentally feasible drop sizes and electric fields will restrict the system to a subset of the  $Ca_E - Re_E$  phase space, thus showing one of the breakup modes, instead of a transition between the two modes. A potential way to observe the transition for the same system is to work with higher molecular weight oils, with viscosity of  $\mathcal{O}(10)$  Pa s, or by increasing the conductivity of both the phases by doping with surfactants, leaving the viscosity and dielectric constants relatively unchanged. Increasing the viscosity or the conductivity of the individual phases ensure that the transition occurs at electric fields of  $\mathcal{O}(kV/cm)$ , with millimeter size drops. Preliminary calculations show that for a drop of polydimethysiloxane (PDMS) in polyisobutylene (PIB), having (M, S, R) = (1, 1, 0.05), the transition in breakup mode can be observed from end-pinching, with a PDMS drop of initial radius 8 mm, subjected to a field of 0.8 kV/cm, to breakup via conical ends with a drop of initial radius 80  $\mu$ m, subjected to a field of 8 kV/cm. However, the drop would take nearly an hour to break because of the high viscosity of the fluids.
## 2.6 Conclusion

We have quantified the effect of surface charge convection on the breakup mode of weakly conducting prolate drops, using the boundary integral method. Prolate drops can support two kinds of flows: directed from the equator to the poles of the drop (prolate A,  $PR_A$  drops), and flows from the poles to the equator (prolate B,  $PR_B$  drops). It has been shown that the breakup mode of a prolate A drop changes from end-pinching to breakup via conical ends beyond a critical  $Re_E$ . The  $Ca_E - Re_E$  parameter space map for two different  $PR_A$  systems (Figures 2.9 and 2.10) show that the critical parameters at which the transition occurs depend on the system under consideration, i. e., (M, S, R) values, however the transition is common to both  $PR_A$  drops. As such, this should be generic to  $PR_A$  drops. Surface charge convection has a less pronounced effect on  $PR_B$  drops. The breakup mode of these drops does not change with increasing  $Re_E$ ; however, the final steady deformation increases when charge convection is included. Similar to  $PR_A$  drops, charge convection reduces the critical capillary number for breakup, and the time at which breakup occurs.

# Chapter 3

# Deformation of a conducting drop in a randomly fluctuating electric field

## 3.1 Introduction

When an electric field is applied around a drop of fluid of initial radius  $a_0$ , suspended in another immiscible fluid, there is a discontinuity in the electric field distribution across the interface due to a mismatch in the electrical properties of the two fluids. As a result, electric stresses are generated at the interface, which deform the drop from an initial spherical shape. The electric stresses are balanced by the capillary stress, which arise due to an interfacial tension,  $\gamma$ . For perfectly conducting or perfectly dielectric drops suspended in a perfectly dielectric liquid, the electric stresses are nonuniform along the interface, and consequently the drop deforms along the direction of the applied field into a prolate shape<sup>17-23</sup>. Understanding how drops respond to an applied electric field is important in applications like electrospray mass spectrometry<sup>1</sup>, electrocoalescence<sup>3,4</sup> and electric field based emulsification<sup>5,6</sup>. For small values of a uniform, direct current (D.C.) applied electric field, Allan and Mason<sup>21</sup> predicted that the steady deformation of a conducting drop in a dielectric liquid,

 ${\mathcal D}$  is proportional to the square of the applied electric field,  $E^*_\infty,$ 

$$\mathcal{D} = \frac{L-B}{L+B} = \frac{9}{16}Ca_E,\tag{3.1}$$

where L and B are the half lengths of the drop along and normal to the direction of the applied electric field, respectively (Figure 3.1), and  $Ca_E = a_0\varepsilon_o E_{\infty}^{*^2}/\gamma$  is the electric capillary number defined as the ratio of electric stresses to capillary stress, with  $\varepsilon_o$  representing the dielectric constant of the medium phase fluid. The electric capillary number can also be defined as the ratio of the capillary time scale,  $t_c = \mu_o a_0/\gamma$  which is the time scale for the capillary stress to restore the drop to the undeformed state, to the flow time scale,  $t_f = a_0/U$ , where the velocity scale,  $U = \varepsilon_o a_0 E_{\infty}^{*^2}/\mu_o$  is obtained by balancing the viscous shear to electric stresses, with  $\mu_o$  denoting the viscosity of the medium phase fluid. To  $\mathcal{O}(Ca_E)$ , the drop deforms to a spheroidal shape.

The small deformation theory given by (3.1) is valid for  $Ca_E \ll 1$ . At larger field strengths, the drop deformation is nonlinear in  $Ca_E$ , and the shape is non-spheroidal<sup>25,27,50</sup>. The inclusion of higher order terms to (3.1) is not sufficient to predict the experimentally observed deformation<sup>28</sup>. The drop ultimately breaks up to form smaller drops beyond a critical value of the electric field. Numerical methods, particularly the boundary integral method and the finite element method, have been employed to calculate the steady nonlinear deformation of drops at larger  $Ca_E$ , and predict the breakup criteria and breakup modes for both uniform<sup>26,29,32,34,48,71</sup> and oscillatory<sup>25</sup> external fields. The manner in which the deformed state is attained, i.e., the transient deformation of the drop, has also been established<sup>72,84,97,98</sup>.

Previous studies have predominantly focused on the transient deformation and breakup of a single drop subjected to a deterministic (uniform or oscillatory) external electric field. In practical systems, the response of a drop will be influenced by the interaction with surrounding drops, interaction with



 $\mu_o, \varepsilon_o, \sigma_o$ 

Figure 3.1: Schematic of the electric field induced deformation of a conducting drop. The axis of symmetry,  $\varphi$ , is along the direction of the electric field,  $E_{\infty}^*$ . The average magnitude of the electric field is  $E_c$ , and the fluctuations are denoted by  $\epsilon^*$ . The drop having viscosity  $\mu_i$ , permittivity  $\varepsilon_i$  and conductivity  $\sigma_i$  is suspended in a dielectric medium with viscosity  $\mu_o$ , permittivity  $\varepsilon_o$  and conductivity  $\sigma_o$ . The initially undeformed state of the drop is shown by the dashed curve. The semi-major and semi-minor axis of the deformed drop are denoted by L and B, respectively. The unit normal (n) and tangential (s)vectors, the continuous tangential coordinate (s), the polar angle  $(\theta)$ , and a fixed source point on the interface (x) are also shown.

walls, and disturbances in operating conditions. For instance, in equipment like electrocoalescers or electro-emulsifiers, the surrounding drops will have different sizes and be randomly distributed around a given ('test') drop. Thus, even when the applied macroscopic voltage (for example, the potential difference across the electrodes in an electrocoalescer) is steady, the behavior of the test drop could be drastically different from the response of a single drop under a deterministic field. An equivalent description of the dynamics of drop deformation and breakup in such practical applications is to quantify drop response to a randomly fluctuating external field. A similar approach has been adopted to study drop fragmentation in mixers and packed beds via experiments<sup>55,56,60</sup>, and simulations<sup>57–60</sup>. In particular, the fluid flow through a dilute fixed bed was modeled as an equivalent anisotropic Gaussian flow field through a spectral expansion method, where the wave number vectors were chosen from statistical distributions to realize a desired flow field. The orientation of tracer polymers, extension of polymer molecules, and droplet breakup in the simulated stochastic flow field was predicted<sup>57–60</sup>. An alternate approach to model a stochastic external flow field was followed by Young and co-workers<sup>61</sup>, where the random component of the flow was modeled as an Ornstein-Uhlenbeck process using a mean, variance, and correlation time. The response of the drop was quantified in terms of a probability distribution function of the final deformation and breakup.

However, to the best of our knowledge, the dynamics of drop deformation and breakup in a random electric field has not been studied before. Therefore, in this chapter, we quantify the transient deformation and breakup of a drop of conducting liquid suspended in a dielectric liquid when subjected to an electric field, the magnitude of which fluctuates randomly in time. We choose the simplest system of a conducting drop, where no sustained fluid flow exists at steady state, to elucidate how fluctuations affect deformation and the criterion for breakup. Again, we emphasize the importance of this problem in the context of practical applications like electrocoalescence and electro-emulsification. A complete description would have to account for many-body hydrodynamic and electrostatic interactions between drops, and spatial fluctuations in the electric field. Nevertheless, our approach is a reasonable first step. We employ small deformation theory and the boundary integral method to predict the effect of fluctuations on the final state of the drop.

## **3.2** Modeling drop deformation and breakup

An uncharged drop of a conducting liquid with initial radius  $a_0$  is suspended in a dielectric medium, as shown in Figure 3.1. The drop and medium phase fluids are density and viscosity matched. The drop is subjected to an electric field, the magnitude of which fluctuates randomly in time, but the direction remains fixed. The electric field deforms the drop from its initial, spherical state. We assume that the deformation is axisymmetric, and quantify effect of fluctuations in the electric field on the transient deformation and criteria for drop breakup. The problem requires the calculation of electric field distribution and fluid flow in the drop and medium phase fluids. Although at steady state there is no fluid flow for conducting drops, the solution to the flow problem is necessary to predict the transient deformation of the drop. We present the governing equations in this section. Henceforth, a superscript '\*' denotes a dimensional variable, and a lack of the superscript denotes a physical parameter, scale, dimensionless group, or the dimensionless version of a dimensional variable.

#### 3.2.1 Statistics of the fluctuating electric field

The external electric field,  $E_{\infty}^{*}$ , is composed of a constant part,  $E_c$ , and a part whose magnitude fluctuates randomly in time,  $\epsilon^{*}$ , i.e.,  $E_{\infty}^{*}(t^{*}) = (E_c + \epsilon^{*}(t^{*}))\hat{e}_z$ , where  $\hat{e}_z$  is the unit vector along the direction of the field. In practice, the fluctuations could be caused by the polydispersity of the system, interaction with surrounding drops, interaction of the drop with walls, or disturbances in operating conditions. Note that we only consider temporal fluctuations of the field, and neglect spatial stochasticity. This assumption is valid when the source of the fluctuations is solely temporal disturbances in operating conditions, or when the concentration of drops in the system is relatively dilute, such that the center-to-center distance between drops is much larger than their radius, and drops do not reorient or experience relative motion due to electrostatic interactions<sup>52</sup>. Instead of determining the contribution of each of the possible factors to the fluctuations in the field, we assume that the random temporal variation of the electric field is described by a stationary Markovian Gaussian process (the Ornstein-Uhlenbeck process)<sup>61,99</sup>. Hence, the evolution of  $\epsilon^*$  follows the stochastic differential equation

$$\frac{d\epsilon^*}{dt^*} = -\lambda^*(\epsilon^* - g_w^*(t^*)), \qquad (3.2)$$

where  $g_w^*$  is the underlying Gaussian white noise driving the fluctuations and  $\lambda^*$  is the inverse correlation time. The fluctuations in the electric field are specified by  $\lambda^*$  and the statistics of  $g_w^*$ . We non-dimensionalize (3.2) using  $E_c$  to scale the electric field, and the capillary time,  $t_c = \mu_o a_0/\gamma$  to scale time, and obtain the dimensionless governing equation for the fluctuations in electric field as

$$\frac{d\epsilon}{dt} = -\lambda(\epsilon - g_w(t)). \tag{3.3}$$

Here,  $\lambda = \lambda^* t_c$  is the dimensionless inverse correlation time. The underlying Gaussian white noise has the properties  $\langle g_w(t) \rangle = 0$ , and  $\langle g_w(t)g_w(t') \rangle = 2G_w \delta(t-t')$ , where  $\delta$  is the Dirac delta function, and  $2G_w$  is the variance of the white noise. A term in the angle brackets denotes an average over an ensemble of initial distribution of the variable. The driven noise is generated using an algorithm described by Fox<sup>99</sup>, after integrating (3.3) to obtain

$$\epsilon(t) = \epsilon_0 e^{-\lambda t} + \int_0^t \lambda e^{-\lambda(t-t')} g_w(t') dt', \qquad (3.4)$$

where,  $\epsilon_0$  is an initial value of the fluctuation. At any given time, the driven noise is Gaussian distributed,  $\epsilon(t) \sim \mathcal{N}(\langle \epsilon_0 \rangle e^{-\lambda t}, G_w \lambda)$ , where  $\mathcal{N}(\overline{\mu}, \nu)$  denotes a normal distribution with mean  $\overline{\mu}$ , and variance  $\nu$ . The distribution of initial value of the fluctuations,  $\epsilon_0$ , is given by

$$\mathcal{P}(\epsilon_0) = \frac{1}{\sqrt{2\pi G_w \lambda}} \exp\left\{-\frac{(\epsilon_0 - \langle \epsilon_0 \rangle)^2}{2G_w \lambda}\right\}.$$
(3.5)

We choose  $\langle \epsilon_0 \rangle = 0$ , so that the mean electric field is set by the constant part,  $E_c$ , and fluctuations to the field is set by the variance of  $\epsilon(t)$ , i.e.,  $G_w\lambda$ . The driven noise has the properties

$$\langle \epsilon(t) \rangle = 0, \tag{3.6}$$

$$\langle \epsilon(t)\epsilon(t')\rangle = G_w\lambda\exp(-\lambda|t-t'|).$$
 (3.7)

where the term  $\langle ... \rangle$  denotes an average over an ensemble of initial distribution of  $\epsilon_0$ , given by (3.5).

It follows from (3.7) that  $\epsilon(t)$  is an exponentially correlated colored noise. Further, the non-dimensional electric field follows a Gaussian distribution at any given time,  $E_{\infty} \sim \mathcal{N}(1, G_w \lambda)$ . A simulated fluctuating electric field signal is shown in Figure 3.2(a) for a specified variance,  $G_w \lambda = 0.1$ . The signal was obtained by taking an average over 100 realizations of the algorithm over the initial distribution given by (3.5). Comparing the statistics of the simulated signal with the statistics predicted theoretically, i.e.,  $E_{\infty} \sim \mathcal{N}(1, G_w \lambda)$  at t = 1, shows that averaging over 100 realizations over (3.5) is sufficient to describe the fluctuating electric field (Figure 3.2(b)).

#### **3.2.2** Small deformation theory

We first consider a slightly spheroidal deformation of the drop surface at small values of the mean electric field (which corresponds to a small value of the mean electrical capillary number). In this limit, the drop can be treated as a sphere during the implementation of the boundary conditions<sup>84,98</sup>. Spherical coordinates are employed and the axis of symmetry is taken along the direction



Figure 3.2: (a) A simulated electric field with variance  $G_w \lambda = 0.1$ . The solid line is an average over 100 realizations of the algorithm over the initial distribution of  $\epsilon_0$ . The dashed line shows the mean value of the fluctuations. (b) Probability density function of the numerically computed (circles) and theoretically predicted (solid line) electric field at t = 1.

of the applied field. The electric field is irrotational, and since the drop is electrically neutral, Gauss's law reduces to the Laplace equation for the inner and outer electrostatic potentials  $(\phi_{i,o}^*)$ , giving

$$\boldsymbol{\nabla}^{*2}\phi_{i,o}^* = 0, \tag{3.8}$$

with the electric field calculated using  $\mathbf{E}_{i,o}^* = -\nabla^* \phi_{i,o}^*$ . The potential in the drop phase,  $\phi_i^*$  is bounded at the center of the drop, and at far field, the potential in the medium phase satisfies  $-\nabla^* \phi_o^* \to \mathbf{E}_{\infty}^*$ . The electric field distribution in the drop and medium is obtained from the solution of (3.8) with these boundary conditions, along with the interface conditions at the surface of the drop,  $r^* = a_0$ , where the potential is continuous

$$\phi_i^* = \phi_o^*, \tag{3.9}$$

and the jump in electric displacement follows

$$\left[-\varepsilon \boldsymbol{\nabla}^* \phi^* \cdot \boldsymbol{n}\right] = q^*(t^*). \tag{3.10}$$

The term in the square brackets in (3.10) represents a difference between inner and outer quantities, n is a unit normal vector, positive in the outward direction (Figure 3.1), and  $q^*$  is the interfacial charge density, which is an unknown. Hence, an additional interface condition to describe the continuity of current across the interface is used. For a perfectly conducting drop, effects of surface charge convection and charge relaxation can be neglected, and the interfacial charge conservation equation reduces to<sup>23,70</sup>

$$\left[\sigma \boldsymbol{\nabla}^* \boldsymbol{\phi}^* \cdot \boldsymbol{n}\right] = 0. \tag{3.11}$$

For a perfectly conducting drop,  $\sigma_i \gg \sigma_o$ , hence (3.11) predicts that the normal electric field inside the drop phase,  $E_{n,i} = 0$ .

After solving the electric field distribution in the two phases, the Maxwell electric stresses at the interface can be calculated using  $\boldsymbol{\tau}_{E_{i,o}}^* = \varepsilon_{i,o} \boldsymbol{E}_{i,o}^* \boldsymbol{E}_{i,o}^* - (\boldsymbol{E}_{i,o}^* \cdot \boldsymbol{E}_{i,o}^*) \boldsymbol{I}/2.$ 

The flow field in the drop and medium phases is governed by the continuity equation and the Navier-Stokes equation,

$$\boldsymbol{\nabla}^* \boldsymbol{\cdot} \boldsymbol{u}_{i,o}^* = 0, \qquad (3.12)$$

and

$$\rho_{i,o}\left[\frac{\partial \boldsymbol{u}_{i,o}^*}{\partial t^*} + \boldsymbol{u}_{i,o}^* \cdot \boldsymbol{\nabla}^* \, \boldsymbol{u}_{i,o}^*\right] = -\boldsymbol{\nabla}^* p_{i,o}^* + \mu_{i,o} \boldsymbol{\nabla}^{*^2} \boldsymbol{u}_{i,o}^*, \quad (3.13)$$

where  $\boldsymbol{u}$  is the velocity and p is the hydrostatic pressure.

We first non-dimensionalize the problem. The electric field is scaled with the constant mean electric field,  $E_c$ . Distance is scaled with the radius of the underformed drop,  $a_0$ . The capillary time,  $t_c$ , is used to normalize time. Interfacial charge density is rendered dimensionless using  $\varepsilon_o E_c$ . Electric stresses  $(\varepsilon_o E_c^2)$  are chosen to scale stresses. The scale for velocity is obtained by balancing electric stresses and viscous stress at the interface, giving  $U = \varepsilon_o E_c^2 a_0/\mu_o$ . These scalings lead to the dimensionless momentum balance,

$$\frac{Re_{i,o}}{\langle Ca_E \rangle} \frac{\partial \boldsymbol{u}_{i,o}}{\partial t} + Re_{i,o} \boldsymbol{u}_{i,o} \cdot \boldsymbol{\nabla} \boldsymbol{u}_{i,o} = -\boldsymbol{\nabla} p_{i,o} + \nabla^2 \boldsymbol{u}_{i,o}, \qquad (3.14)$$

where  $Re_{i,o} = \rho_{i,o}\varepsilon_o E_c^2 a_0^2/\mu_{i,o}^2$  is the Reynolds number, and  $\langle Ca_E \rangle = a_0\varepsilon_o E_c^2/\gamma$ is the mean electric capillary number. We assume creeping flow,  $Re_{i,o} \ll 1$ , and further assume that  $Re_{i,o}/\langle Ca_E \rangle \ll 1$  to reduce the momentum balance to

$$-\boldsymbol{\nabla}p_{i,o} + \nabla^2 \boldsymbol{u}_{i,o} = 0. \tag{3.15}$$

Since the problem is axisymmetric, (3.15) can be solved using a streamfunction  $\psi$ , which automatically satisfies the incompressibility (3.12). The streamfunction satisfies the biharmonic equation

$$D^4 \psi_{i,o} = 0, (3.16)$$

where  $D^4 = D^2(D^2)$ , and  $D^2 = \partial^2/\partial r^2 + (\sin \theta/r^2) \{\partial/\partial \theta [(1/\sin \theta)\partial/\partial \theta]\}$ . The velocity is related to the streamfunction through

$$\boldsymbol{u}_{i,o} = \boldsymbol{\nabla} \times \left[ \frac{\psi_{i,o}}{r \sin \theta} \hat{\boldsymbol{e}}_{\boldsymbol{\phi}} \right], \qquad (3.17)$$

where  $\hat{\boldsymbol{e}}_{\phi}$  is the unit vector in the azimuthal direction. The flow field is subject to the constraints that the velocity at the center of the drop is bounded, and the far field condition in the medium,  $\boldsymbol{u}_o = 0$  at  $\boldsymbol{r} \to \infty$ . The complete solution requires four more interface conditions. At small field strengths where  $\langle Ca_E \rangle \ll 1$ , the interface is only slightly deformed, and the instantaneous shape can be described using<sup>84,98</sup>

$$\xi = 1 + \frac{2}{3}\mathcal{D}(t)(3\cos^2\theta - 1), \qquad (3.18)$$

where  $\mathcal{D}(t)$  is the instantaneous deformation of the drop, defined as the ratio of the difference in semi-major and semi-minor axis of the drop to the sum of the semi-major and semi-minor axis. In the limit of small deformation  $(\langle Ca_E \rangle \ll 1)$ , the interface conditions

$$u_{\theta,i} = u_{\theta,o} \tag{3.19}$$

and

$$u_{r,i} = u_{r,o} = \frac{1}{\langle Ca_E \rangle} \frac{d\xi}{dt}$$
(3.20)

can be applied at r = 1, and the deformation subsequently calculated using the interfacial stress balance equation, which in the absence of surfactant reads

$$(p_i - p_o)\boldsymbol{n} + (\boldsymbol{\tau}_{H,o} - M\boldsymbol{\tau}_{H,i}) \cdot \boldsymbol{n} + [\boldsymbol{\tau}_{E_{i,o}} \cdot \boldsymbol{n}] = \frac{1}{\langle Ca_E \rangle} (\boldsymbol{\nabla}_s \cdot \boldsymbol{n}) \boldsymbol{n}. \quad (3.21)$$

Here,  $\tau_H$  represents the deviatoric stress tensor, and  $\nabla_s \cdot n$  is the curvature of the interface where  $\nabla_s$  is the surface gradient operator, defined as  $\nabla_s = (I - nn) \cdot \nabla$ . A detailed procedure of solution of the equations can be found in Ref.<sup>98</sup>, and an overview of the procedure is presented in this work. The general solution of the flow field is obtained from (3.16) and (3.17), and the constants are rewritten in terms of the instantaneous deformation,  $\mathcal{D}(t)$ using the constraints of bounded flow at the drop center, far field condition, interfacial velocity (3.19) and (3.20), and the tangential stress balance obtained from (3.21). The normal stress balance is then used to obtain the governing equation for transient deformation,

$$\tau \frac{d\mathcal{D}}{dt} + \mathcal{D} = \mathcal{D}_{DC}(1 + \epsilon(t)^2), \qquad (3.22)$$

where  $\tau = \frac{(19M + 16)(2M + 3)}{40(M + 1)}$ ,  $M = \mu_i/\mu_o$  and  $\mathcal{D}_{DC} = 9\langle Ca_E \rangle/16$  is the steady deformation of a conducting drop in a dielectric medium under a uniform D.C. electric field at small electric field strengths<sup>21,22</sup>. Integrating (3.22), we obtain the instantaneous deformation of a conducting drop in a randomly fluctuating field,

$$\mathcal{D}(t) = \mathcal{D}_{DC}(1 - e^{-t/\tau}) + \frac{\mathcal{D}_{DC}}{\tau} \int_0^t \left[ 2\epsilon(t')e^{-(t-t')/\tau} + \epsilon(t')^2 e^{-(t-t')/\tau} \right] dt'.$$
(3.23)

The first term on the right-hand side is the expression of the transient deformation of a drop under a uniform D.C. field when transient fluid inertia can be neglected, i.e., the flow is established instantaneously on the timescale the interface deforms<sup>84,97,98</sup>. This predicts that the deformation monotonically settles towards the steady state result given in (3.1) as  $t \to \infty$ . The second term represents the contribution of the fluctuations in the electric field to the transient deformation. Note that fluctuations lead to  $\mathcal{D}(t)$  being non-local in time; the history of the electric field is remembered through the correlation time. A closed form solution of  $\mathcal{D}(t)$  cannot be obtained because a closed form expression of  $\epsilon(t)$  is not known. Therefore, we obtain the statistics (mean and variance) of the instantaneous deformation as

$$\langle \mathcal{D}(t) \rangle = \mathcal{D}_{DC}(1 + G_w \lambda)(1 - e^{-t/\tau})$$
(3.24)

and

$$var(\mathcal{D}(t)) = \frac{\mathcal{D}_{DC}^2 G_w \lambda}{\tau} (2 + G_w \lambda) (1 - e^{-2t/\tau}).$$
(3.25)

Clearly, the mean deformation of a drop in a randomly fluctuating field is greater than under a uniform D.C. field when the field strength is small, and the difference in deformation increases with fluctuations in the field  $(G_w\lambda)$ . When the fluctuations vanish, i.e.  $G_w\lambda \to 0$ , the electric field around the drop assumes the form of a steady D.C. field. In this limit, we find that  $\langle \mathcal{D}(t) \rangle = \mathcal{D}_{DC}(1 - e^{-t/\tau})$ , and  $var(\langle \mathcal{D}(t) \rangle) = 0$ , which is the expected result for drop deformation under a steady electric field.

#### **3.2.3** Boundary integral formulation

The nonlinear deformation at a larger value of the mean electric field, and possible breakup is predicted using the boundary integral method. This requires the solution of the electric field and fluid flow at the interface only, thereby reducing the dimensionality of the problem by one, and consequently reducing the computational  $\cot^{77-79}$ . The Laplace equation (3.8) is recast into a non-dimensional integral equation at the interface<sup>32,34,67,81</sup>,

$$\frac{S-1}{4\pi S} \oint_{A} \frac{\boldsymbol{r} \cdot \boldsymbol{n}(\boldsymbol{x})}{r^{3}} E_{n,o}(\boldsymbol{y}) dA(\boldsymbol{y}) + \frac{S+1}{2S} E_{n,o}(\boldsymbol{x}) = \mathbf{E}_{\infty} \cdot \boldsymbol{n}(\boldsymbol{x}) - \frac{1}{4\pi S} \oint_{A} q(\boldsymbol{y}) dA(\boldsymbol{y}) + \frac{1}{2S} q(\boldsymbol{x}).$$
(3.26)

where  $S = \varepsilon_i/\varepsilon_o$  is the ratio of dielectric constant of the drop to medium phase fluid,  $\mathbf{r} = \mathbf{y} - \mathbf{x}$  is the difference between an observer point  $\mathbf{y}$  that can move along the interface and a fixed source point  $\mathbf{x}$  on the interface. The integral is taken over the surface area, A of the drop. The normal electric field in the drop phase is calculated using the dimensionless form of (3.11),  $E_{n,i} = RE_{n,o}$ , where  $R = \sigma_o/\sigma_i$  is the ratio of electrical conductivity of the medium to drop phase fluid. For a conducting drop in a dielectric,  $\sigma_i \gg \sigma_o$ , hence  $E_{n,i} = 0$ ; however in the computations, instead of prescribing  $E_{n,i} = 0$ , we specify a very small value of  $R (\approx 10^{-10})$ . The interface is initially uncharged, hence the normal electric field can be computed at t = 0. The tangential field is obtained by an integral transform of the Laplace equation in terms of the electrostatic potential,  $\phi_o^{34,67,82}$ 

$$\phi_o(\boldsymbol{x}) = \phi_\infty(\boldsymbol{x}) + \oint_A \frac{1}{4\pi r} (E_{n,o}(\boldsymbol{y}) - E_{n,i}(\boldsymbol{y})) dA(\boldsymbol{y}), \qquad (3.27)$$

and using the relation  $E_{t,o} = -\partial \phi_o / \partial s$  and (3.9). Here, s is the tangential coordinate measured from  $\theta = 0$  (Figure 3.1), and  $E_{t,o} = \mathbf{E}_o \cdot \mathbf{t}$ . From the distribution of the electric field in the drop and medium, the jump in electric stresses at the interface is calculated, which in non-dimensional form reads

$$[\boldsymbol{\tau}_{E} \cdot \boldsymbol{n}] = \frac{1}{2} [(E_{n,o}^{2} - SE_{n,i}^{2}) + (S-1)E_{t,o}^{2}]\boldsymbol{n} + E_{t,o}(E_{n,o} - SE_{n,i})\boldsymbol{t} = \Delta p_{E}\boldsymbol{n} + qE_{t,o}\boldsymbol{t}.$$
(3.28)

For a conducting drop,  $E_t = 0$ , and  $E_{n,i} = 0$ , and (3.28) reduces to  $[\boldsymbol{\tau}_E \cdot \boldsymbol{n}] = (E_{n,o}^2/2)\boldsymbol{n}.$ 

The Stokes equations (3.15) can be cast as an integral equation in dimensionless form<sup>83</sup>, and when the drop and medium are viscosity matched this yields

$$\boldsymbol{u}_{\boldsymbol{o}}(\boldsymbol{x}) = -\frac{1}{8\pi} \oint_{A} \Delta \boldsymbol{f}(\boldsymbol{y}) \cdot \boldsymbol{J}(\boldsymbol{y}, \boldsymbol{x}) dA(\boldsymbol{y}), \qquad (3.29)$$

where J denotes the free-space Green's functions for velocity, and  $\Delta f(y)$  is the jump in hydrodynamic stresses at the observer points on the interface, calculated using (3.21).

After obtaining the electric field and interfacial velocity, the interfacial charge is updated using the dimensionless form of (3.10),

$$q = E_{n,o} - SE_{n,i}.$$
 (3.30)

Finally, the interface is updated using the dimensionless kinematic condition

$$\frac{d\boldsymbol{x}}{dt} = \langle Ca_E \rangle (\boldsymbol{u_o} \cdot \boldsymbol{n}) \boldsymbol{n}.$$
(3.31)

#### **3.2.4** Numerical scheme

An initial value for the fluctuations in the electric field,  $\epsilon_0$ , is chosen from the distribution given by (3.5). Equations (3.26), (3.27) and (3.29) are solved sequentially. The details of the numerical scheme have been provided before<sup>34,67</sup>, and are briefly reviewed here. The field and flow are assumed to be axisymmetric, which allows an analytical integration over the azimuthal direction, reducing surface integrals to line integrals over the contour of the drop. The top half of the drop is divided into N elements, creating N + 1 nodes. The nodes are called source points, and their coordinates are denoted by  $\boldsymbol{x}$  (Figure 3.1). All variables of interest are interpolated as cubic splines with respect to the arc length, s. The integral over the contour of the drop is expressed as a sum of integrals over each element. Singular terms in the integrand are

subtracted out, and then added back, following standard regularization techniques<sup>82</sup>. The integrals are evaluated using Gauss-Legendre quadrature. The points at which the integral is evaluated are referred to as observer points, and their coordinates are denoted by  $\boldsymbol{y}$ . After the electric field and fluid flow is calculated, the surface charge density (3.30) and shape of the interface (3.31) are updated, the latter using the second-order Runge-Kutta method, and the deformation is calculated. The fluctuation in the electric field at the next time step is then calculated from (3.4) using the algorithm given in Ref.<sup>99</sup>, and is used to update the boundary value of  $E_{\infty}$  in (3.26).

The time step of the Runge-Kutta method and N are chosen to ensure that the volumetric flow rate across the interface, which should identically be zero to conserve mass, is at most  $\mathcal{O}(10^{-6})$  for the initial 20 iterations. This ensures numerical stability of the computations. If the volumetric flow rate across the interface remains  $\mathcal{O}(10^{-6})$  or less, while the maximum value of the radial velocity keeps on decreasing, and reaches  $\mathcal{O}(10^{-4})$  or less, we conclude that the drop has attained a steady shape. If the volumetric flow rate slowly starts to increase, along with an increase in the maximum value of the radial velocity, we conclude that the drop shape will be unsteady, and it will result in break up. The boundary integral method cannot track the interface after the drop breaks; in this case, the results are reported at a time instant very close to breakup, where the ratio of volumetric flow rate across the interface to the initial volumetric flow rate is 100. Some computations predicted drop shapes that were not fore-aft symmetric. This occurred when the electric field fluctuated by a large magnitude in one time step, causing numerical errors. The results of these computations were discarded. For all our computations, the top half of the drop was divided into 150 elements, and the time step size was taken to be 0.02. These values were chosen after performing a convergence analysis, the results of which are given in Appendix B.

Table 3.1: Physical properties of the fluids used. The interfacial tension between the fluids is  $\gamma = 17 \text{ mN/m}^{48}$ . The drop phase corresponds to system (G10) of Karyappa *et al.*<sup>48</sup>. Here  $\varepsilon_r$  denotes the dielectric constant.

Fluid	$\sigma$ (S/m)	$\varepsilon_r$	$\mu$ (Pa s)	$ ho~({ m kg/m^3})$
Glycerol	$7.8 \times 10^{-2}$	40	0.76	1256
Castor Oil	$4 \times 10^{-11}$	4.9	0.79	970

After performing one computation for the final state of the drop using a given initial value of  $\epsilon_0$ , the numerical scheme is repeated for several other initial values of  $\epsilon_0$  taken from the distribution (3.5). The transient deformation of the drop, and the final state of the drop are reported as an average over this ensemble of initial values of  $\epsilon_0$ . For this work, the computations were performed for 100 different initial values of the fluctuation in the electric field.

## **3.3** Drop deformation and breakup

We select parameter values corresponding to a drop of glycerol with 5M sodium chloride, having an initial radius  $a_0 = 0.5$  mm suspended in castor oil. The physical properties of the system can be found in Ref.<sup>48</sup>, and are listed in Table 3.1. For this combination of fluids, the ratios of physical properties are M = 0.96, S = 8.16 and  $R = 5.1 \times 10^{-10}$ . Since the two fluids are nearly viscosity matched, we take M = 1 in the computations. At the highest electric field strength chosen in this work,  $Re_i = 6 \times 10^{-3}$ ,  $Re_o = 4 \times 10^{-3}$ , and for any field  $Re_{i,o}/\langle Ca_E \rangle < 10^{-2}$ . This justifies the assumptions in reducing the Navier-Stokes equation to the Stokes equations.

#### 3.3.1 Constant electric field

We first evaluate the response of the drop to a uniform D.C. electric field. When the applied field is such that the electric capillary number  $Ca_E \leq 0.21$ , the drop deforms to a steady spheroidal shape, as shown in Figure 3.3. The steady deformation increases with an increase in  $Ca_E$  because of an increase in the strength of the electric stresses. At  $Ca_E \approx 0.21$  the electric stresses become large enough to overcome capillary stresses, and cause the drop to undergo breakup. As shown in the inset of Figure 3.3, the drop breaks up with the formation of pointed ends for all  $Ca_E > 0.21$ . This predicted critical  $Ca_E$ for breakup is similar to the values reported earlier for conducting drops<sup>48,100</sup>.



Figure 3.3: Deformation plotted as a function of the electric capillary number. For drops that deform to a steady shape, the deformation corresponds to the steady final deformation. For drops that undergo breakup, the deformation corresponds to the deformation before breakup. The insets show the final shapes of a drop that reaches a steady shape, and a drop that breaks up with pointed ends. The vertical line demarcates the transition of the system from a steady final state to breakup by pointed ends. The critical electric capillary number for the transition is  $Ca_E \approx 0.21$ .

## 3.3.2 Comparison of small deformation theory to boundary integral computations

We first predict the transient deformation of a drop under small electric fields, and compare the results from boundary integral computations to the small deformation theory. Figure 3.4 shows the result at a mean electric capillary number,  $\langle Ca_E \rangle = 0.01$ , and a variance in the fluctuations,  $G_w \lambda = 0.1$ . The computations involve selecting an initial value for the fluctuations in the electric field,  $\epsilon_0$ , from the distribution given by (3.5), and calculating the transient deformation for the chosen  $\epsilon_0$ . Each light gray curve in Figure 3.4 corresponds to the computed transient deformation for a given  $\epsilon_0$ . After computing the deformation for 100 different values of  $\epsilon_0$ , an average is taken over the ensemble of initial distribution, and is shown by the solid curve. The mean transient deformation,  $\langle \mathcal{D}(t) \rangle$  predicted by the small deformation theory in (3.24) is shown by the dashed curve in Figure 3.4. The mean deformation obtained from the boundary integral computations match the predictions of the small deformation theory. Moreover, nearly all the transient deformation curves obtained for a given  $\epsilon_0$  from the computations lie within one standard deviation from the mean predicted by the small deformation theory, shown by the dash-dotted lines in Figure 3.4. This verifies that the numerical scheme we use in the computations is accurate.

For comparison, the transient deformation of the drop under a steady D.C. electric field at  $Ca_E = 0.01$  is shown by the dotted line in Figure 3.4. Both the computations and the small deformation theory predict that the final steady deformation of the drop under a fluctuating electric field is greater than the deformation under a constant field. The small deformation theory, (3.24), predicts this difference in the final steady deformation to be proportional to the fluctuations in the electric field. Comparing the final steady deformation,



Figure 3.4: Transient deformation of the drop at a mean electric capillary number  $\langle Ca_E \rangle = 0.01$  and variance in the fluctuations  $G_w \lambda = 0.1$ . The light gray curves correspond to the transient deformation for a given initial value of the fluctuation in electric field,  $\epsilon_0$ , calculated using boundary integral computations. The solid curve is calculated as the average of the gray curves, and represents the average transient deformation taken over 100 values of  $\epsilon_0$ . The dashed curve corresponds to the average transient deformation,  $\langle \mathcal{D}(t) \rangle$ , calculated using the small deformation theory (3.24). The dash-dotted curves predict the deformation one standard deviation from the mean, obtained from the small deformation theory (3.25). The dotted curve shows the transient deformation of the drop under a steady D.C. field at  $Ca_E = 0.01$ , calculated using boundary integral computations.

we find that  $\langle \mathcal{D}(t) \rangle - \mathcal{D}_{DC} = 8 \times 10^{-4} \sim \mathcal{O}(\mathcal{D}_{DC}G_w\lambda)$ , as predicted by (3.24). This difference increases as the fluctuations grow stronger. The fluctuations increase as the variance of the underlying white noise,  $G_w$ , increases, or as the correlation time  $\lambda^{-1}$  decreases. A higher variance increases the spread of the electric field around the mean. A reduction in the correlation time implies that the fluctuations have less memory of their history, and can suddenly grow from values less than the mean to values greater than the mean. Hence, the probability of the drop being exposed to larger fields increases with the strength of the fluctuations. The deformation of the drop scales quadratically with the electric field,  $E_{\infty}^2$ ; hence, the net effect of the fluctuations about the mean field will not negate each other, and the mean deformation under a fluctuating field will be different from that under a constant field. The drop is exposed to fields both larger and smaller than the mean field, driven by the fluctuations. On an average, the effects under the larger fields dominate, and the mean final deformation of the drop is greater than the deformation under a constant electric field. The net effect of fluctuations in the electric field is to deform a drop more than a steady D.C. field.

#### 3.3.3 "Low" mean electric capillary number

Next we calculate the deformation of the drop at a "low" mean electric capillary number, where the small deformation theory is not valid, yet which are smaller than the critical electric capillary number for breakup under a steady field ( $Ca_E = 0.21$ ). Figure 3.5(a) shows the transient deformation of a drop at  $\langle Ca_E \rangle = 0.1$  and  $G_w \lambda = 0.1$ . Akin to Figure 3.4, the light gray curves correspond to computations for a given initial value of the electric field fluctuation  $\epsilon_0$ , and the solid black curve represents the average transient deformation over 100 values of  $\epsilon_0$ . The dotted curve shows the transient deformation under a steady D.C. electric field for  $Ca_E = 0.1$ . The computations were performed till twice the time taken for the drop to reach steady state under a steady field. For all values of  $\epsilon_0$ , the computations predict a steady deformation of the drop. Similar to the observations at small deformation, the mean deformation under a fluctuating electric field is greater than under a steady electric field. This is further shown by plotting the probability density function of the final deformation  $(\mathcal{D}(t=25))$  of the drop (Figure 3.5(b)). The deformation scales nonlinearly with the applied field, therefore the distribution function is not

Gaussian. The dashed curve was obtained by fitting a mixture of two normal distributions to the final deformation, and is shown in the figure to guide the eye. Clearly, fluctuations in the electric field increase the mean deformation of the drop.

#### 3.3.4 "High" mean electric capillary number

The system considered undergoes breakup with pointed ends at  $Ca_E = 0.21$ when subjected to a constant electric field. We investigate the system at  $\langle Ca_E \rangle = 0.28$  and  $G_w \lambda = 0.1$  to determine the effect of fluctuations on breakup. The transient deformation for a given  $\epsilon_0$  is shown by the light gray curves, and the average over 100 values of  $\epsilon_0$  is shown by the solid curve in Figure 3.6(a). The computations were performed till twice the breakup time for the drop under a constant field, and predict breakup with pointed ends for all values of  $\epsilon_0$ . The point where the curves terminate denotes the point of breakup for a given  $\epsilon_0$ . The average transient deformation curve is plotted till the mean breakup time obtained from the individual gray curves. The average deformation of the drop before breakup is greater than the deformation under a steady electric field at all given times leading to breakup. More prominently, the mean breakup time under a fluctuating electric field is less than the breakup time under a steady field, as shown by the dotted curve in Figure 3.6(a). The probability density function of the breakup time is shown in Figure 3.6(b), with the breakup time under a constant field shown by the solid line. The breakup time does not follow a universal distribution for different  $\langle Ca_E \rangle$ ; hence, a mixture of two normal distribution functions was fit to the probability density function and is shown by the dashed curve to guide the eye. Fluctuations in the electric field act to increase the average deformation by subjecting the drop to fields greater than the mean, which increases



Figure 3.5: (a) Transient deformation of a drop at  $\langle Ca_E \rangle = 0.1$  and  $G_w \lambda = 0.1$ . The light gray curves correspond to the transient deformation for a given initial value of the fluctuation in electric field,  $\epsilon_0$ , calculated using boundary integral computations. The solid curve is calculated as the average of the gray curves, and represents the average transient deformation taken over 100 values of  $\epsilon_0$ . The dotted curve shows the transient deformation of the drop under a steady D.C. field at  $Ca_E = 0.1$ . (b) Probability density function of the final deformation of the drop. The dashed curve is a fit of a mixture of two normal distributions to the probability density function. The solid line shows the final deformation of the drop under a steady D.C. electric field. The top-right inset shows the mean deformed steady state of the drop at t = 25, with the initial state shown by the dashed circle for reference.

the rate of deformation. Although fluctuations also reduce the field from the mean value, the additional deformation due to an exposure to higher fields



dominate, and consequently the drop is driven to breakup faster than under a constant field.

Figure 3.6: (a) Transient deformation of a drop at  $\langle Ca_E \rangle = 0.28$  and  $G_w \lambda = 0.1$ . The light gray curves correspond to the transient deformation for a given initial value of the fluctuation in electric field,  $\epsilon_0$ , calculated using boundary integral computations. The solid curve is calculated as the average of the gray curves, and represents the average transient deformation taken over 100 values of  $\epsilon_0$ . The dotted curve shows the transient deformation of the drop under a steady D.C. field at  $Ca_E = 0.1$ . (b) Probability density function of the breakup time of the drop. The dashed curve is a fit of a mixture of two normal distributions to the probability density function. The solid line shows the breakup time of the drop under a steady D.C. electric field. The top-right inset shows the mean shape of the drop before breakup at the point where the solid curve in (a) terminates, with the initial state shown by the dashed circle for reference.

### 3.3.5 "Intermediate" mean electric capillary number

We next study the system at mean electric capillary numbers slightly less than the critical capillary number for breakup. Figure 3.7(a) shows the transient deformation at  $\langle Ca_E \rangle = 0.19$  and  $G_w \lambda = 0.1$ . The drop is predicted to reach a steady deformed shape under a constant electric field, the transient deformation of which is shown by the dotted curve. When the field fluctuates, there are two populations for the final state of the drop. For certain values of the initial fluctuations in the field,  $\epsilon_0$ , the drop attains a deformed state at a time which is twice the time to reach steady deformation under a constant field. This set of drops is represented by the light gray curves in Figure 3.7(a). For other values of  $\epsilon_0$ , the computations predict drop breakup by pointed ends. This set is shown by the dark gray curves. The solid black curve represents the average over the light gray curves, and is the average transient deformation of the population of drops that do not undergo breakup throughout the time the computations were performed. The dashed curve denotes the average transient deformation of the population of drops that breakup with pointed ends. The probability density function of the deformation of the drops is shown in Figure 3.7(b). For drops that attain a steady deformed state, the deformation at t = 45, i.e., the time till which the computations were performed is taken, and for drops that undergo breakup, the final deformation before breakup is taken for calculating the probability distribution. The distribution is bimodal with one peak corresponding to the mean deformation of drops that maintain a stable deformed state, and another peak at the average deformation of the drops before breakup.

At intermediate values of the mean electric capillary number, fluctuations in the electric field can drive the field to values greater than the critical electric field. Depending on the amount of time the drop is subjected to these larger



Figure 3.7: (a) Transient deformation of a drop at  $\langle Ca_E \rangle = 0.19$  and  $G_w \lambda = 0.1$  calculated using boundary integral computations. The light gray curves correspond to the transient deformation for initial values of the fluctuation in electric field,  $\epsilon_0$ , which predict steady deformation. The dark gray curves correspond to the transient deformation for  $\epsilon_0$  values that predict breakup. The solid curve is calculated as the average of the light gray curves, and the dashed curve is calculated as the average of the dark gray curves. The dotted curve shows the transient deformation of the drop under a steady D.C. field at  $Ca_E = 0.19$ . (b) Probability density function of the final deformation (for drops reaching steady state) or final deformation before breakup (for drops that undergo breakup). The dashed curve is a fit of a mixture of two normal distributions to the probability density function. The insets show the mean drop shape at steady state (t = 45) and just before breakup (the point where the dashed curve in (a) terminates), with the shape of the undeformed drop at t = 0 shown by the dashed circles for reference.

electric fields, it may undergo breakup, or subsequently remain stable if the fluctuations lower the field back to sub-critical values. All computations under random fields were performed till a time which is twice the time for a drop to reach steady state, or twice the time to undergo breakup under a constant electric field. From Fig 3.7(a) it follows that some of the drops that are predicted to attain a stable deformed state at t = 45 could undergo breakup if the computations were run longer. The transition of the drop from a steady deformed state to a state of breakup does not occur at a distinct electric capillary number due to fluctuations in the electric field.

Droplet breakup at sub-critical capillary numbers was also observed in model stochastic flow fields, and the criterion for breakup was found to depend on the transient nature of the field [59, 60]. To quantify the effect of the strength of fluctuations on the transition to bimodal states and breakup, we plot the percentage of drops undergoing breakup as a function of  $\langle Ca_E \rangle$ for different values of  $G_w\lambda$ . The percentage is calculated as the fraction of the computations with a given initial fluctuation in the field ( $\epsilon_0$ ) predicting breakup. The result is shown in Fig. ??. When the external field is steady, characterized by  $G_w \lambda = 0$ , there is a sharp transition at  $\langle Ca_E \rangle = 0.21$  from steady deformation to drop breakup, as shown by the solid curve. Fluctuations in the electric field soften this transition by instantaneously subjecting the drop to an electric field greater than the critical value, even when the mean field is sub-critical. As a result, instances of drop breakup are observed over a range of  $\langle Ca_E \rangle$ , instead of a distinct critical  $\langle Ca_E \rangle = 0.21$ . The fraction of drops that undergo breakup at a given  $\langle Ca_E \rangle$  increases with the strength of fluctuations. Large fluctuations, quantified by a larger value of  $G_w\lambda$  have a higher probability of driving the electric field to values greater than the critical for a given  $\langle Ca_E \rangle$ , compared to weaker fluctuations. As shown in Fig. ??, at  $\langle Ca_E \rangle = 0.18, 22\%$  drops undergo breakup for  $G_w \lambda = 0.1$ , while 5% drops

undergo breakup at the same  $\langle Ca_E \rangle$  when  $G_w \lambda = 0.001$ . When  $G_w \lambda = 0.1$ , all the drops were predicted to undergo breakup at  $\langle Ca_E \rangle > 0.21$ . For weaker fluctuations, not all drops are observed to undergo breakup within the time of the computations. This fraction would eventually breakup if the computations were allowed to run longer. Weaker fluctuations are characterized by a longer correlation time, or a stronger memory of the fluctuation history. Hence, when fluctuations reduce the field to sub-critical values, the field remains at those values for a longer period of time. Consequently, for the drops where this occurs, the breakup time for the individual drop would be longer. The mean breakup time for the population that breaks up is still smaller than the breakup time under constant fields. Moreover, since the mean field is greater than the critical, all the drops would eventually undergo breakup.

## 3.4 Discussion

The softening in transition from steady deformation to drop breakup due to increasing fluctuations in the electric field is analogous to the coil-stretch transition of polymers in an external flow field<sup>57,58,101–105</sup>. When subjected to an external flow field, a polymer molecule gets stretched from an initial configuration. The specific initial configuration of a polymer molecule, termed molecular individualism<sup>101</sup>, is determined from a random thermal equilibration process, and dictates the rate of extension of the molecule. Similarly, the transient deformation of a drop under a random electric field follows a trajectory based on the initial random fluctuation,  $\epsilon_0$ ; thus the time to reach steady state or to breakup is different for an individual drop. The extension of a polymer molecule depends on the strength and nature of the flow field. In a pure extensional flow, a polymer molecule exhibits a sharp transition at a critical value of the dimensionless flow strength from a coiled state, where



Figure 3.8: Percentage of drops that undergo breakup as a function of the mean electric capillary number for  $G_w\lambda = 0.001(\diamondsuit), 0.01(\Box)$  and  $0.1(\circ)$ . The solid curve corresponds to a steady D.C. electric field. The dashed, dotted, and dash-dotted curves are drawn to guide the eye. Based on the strength of the fluctuations and  $\langle Ca_E \rangle$ , three final states are identified - all the drops reach steady deformation; some drops reach steady state and some undergo breakup; and all drops undergo breakup.

the extension is relatively low, to a stretched state characterized by a high extension approaching the contour length. The molecule tends to align along the extensional axis of the flow, and may be driven out of this axis by Brownian motion into a coiled state. Beyond a critical value, the flow is strong enough to overcome Brownian forces and result in a stretched configuration. The addition of a rotational component to the external flow diminishes the sharpness of this transition. In addition to Brownian forces, the vorticity of the external flow can also drive the polymer away from the extensional eigenvectors of the flow into orientations where the flow exerts less stretching force, thereby reducing the sharpness in transition. The fluctuations in the electric field play a role analogous to Brownian forces and the rotational component of the flow field, by driving the electric field to values greater than the critical field, even when the mean field is sub-critical, or to values smaller than the critical field when the mean field is super-critical. As a result, the transition from exclusively steady deformation to breakup occurs gradually over a range of  $\langle Ca_E \rangle$ .

The source of fluctuations in real systems could be the presence of multiple drops of different size at different positions with respect to the test drop, interaction with walls, or disturbances in operating conditions. The strength of the fluctuations would depend on the polydispersity of the system, concentration of drops, and the magnitude of disturbances. As such, determining operating conditions based on the response of a single drop under a well-defined external field can lead to unexpected results. For instance, in electrocoalescers, where electric fields are employed to demulsify oil-water systems, an operating electric would be set to maximize the frequency of collision of drops, without causing breakup. The collision frequency, and the separation efficiency increases with electric field strength<sup>106</sup>; hence, a natural choice is to set the electric field to a large value, yet less than the critical field for breakup. We show here that fluctuations can cause certain fraction of drops to breakup even at sub-critical fields, which is undesirable for coalescence. The electric capillary number scales as the square of the electric field, hence even at fields sufficiently lower than the critical, drop breakup might occur. For the system studied, drop breakup can start at  $\langle Ca_E \rangle = 0.15$  depending on the strength of the fluctuations. This corresponds to a decrease in the critical electric field for breakup from 4.1 kV/cm to 3.4 kV/cm. On the contrary, the effect of fluctuations can be desirable in applications where emulsifying immiscible liquids is the  $goal^5$ . A lower electric field can be employed to create an emulsion. Conversely, at the same electric field, the emulsification can take place faster because of the reduction in the average breakup time of drops under

fluctuating fields.

## 3.5 Conclusion

We have studied the dynamics of a conducting drop suspended in a dielectric liquid under a randomly fluctuating electric field. The transient deformation of the drop was first predicted using a small deformation theory where the mean electric capillary number is small ( $\langle Ca_E \rangle \ll 1$ ). The mean deformation and variance in deformation were predicted, and the expressions were found to match the results for drop deformation under a constant field in the limit of zero fluctuations. Nonlinear deformation and breakup were predicted using boundary integral computations, which were validated using the small deformation theory.

The random electric field is specified by its mean, which sets  $\langle Ca_E \rangle$ , and its variance,  $G_w \lambda$ , which denotes the strength of fluctuations. The net effect of fluctuations at any  $\langle Ca_E \rangle$  is to increase the deformation of the drop compared to the deformation under a constant field. The extent of the increase in deformation depends on the strength of the fluctuations. When  $\langle Ca_E \rangle$  is greater than the critical electric capillary number for breakup, the increased deformation manifests as a decrease in the time taken for the drop to undergo breakup. More interestingly, at  $\langle Ca_E \rangle$  slightly less than the critical value, there exists two populations of drops, one that attains a steady deformed state and another that undergoes breakup. The range of  $\langle Ca_E \rangle$  for which this bimodal distribution is observed depends on the strength of the fluctuations.

## Chapter 4

# Effective viscosity of a dilute emulsion of spherical drops containing soluble surfactant

## 4.1 Introduction

The flow of emulsions of an immiscible fluid in another fluid is encountered in food, petroleum, and pharmaceutical processing industries. Thus, it is important to predict the rheological properties of these systems. Einstein<sup>107,108</sup> was the first to calculate the effective viscosity of a dilute suspension of rigid spheres in a Newtonian fluid, subjected to a linear creeping flow. He found that the suspension behaves as a Newtonian fluid, with an effective viscosity greater than the viscosity of the suspending fluid ( $\mu$ ). Specifically,

$$\frac{\mu_E}{\mu} = 1 + \frac{5}{2}\phi, \tag{4.1}$$

where  $\mu_E$  is the effective viscosity of the suspension, and  $\phi$  is the volume fraction of the suspended rigid spheres. Taylor<sup>109</sup> obtained an expression for the effective viscosity of a dilute emulsion of spherical drops of a Newtonian fluid suspended in another Newtonian fluid by accounting for viscous dissipation of energy due to flow inside the drops. Taylor's result is

$$\frac{\mu_T}{\mu} = 1 + \left(\frac{5M+2}{M+1}\right)\frac{\phi}{2},\tag{4.2}$$

where  $\mu_T$  is the effective viscosity of the emulsion, and M is the ratio of the viscosity of the drop to the viscosity of the suspending medium. Einstein's expression is recovered from (4.2) in the limit  $M \to \infty$ . Interestingly, for a suspension of bubbles  $(M \to 0)$  there is still a positive viscosity correction due to interfacial tension. There have been numerous extensions to the works of Einstein and Taylor; we will not attempt to survey the extensive literature here.

Emulsions often contain surfactants, which are added to maintain stability of the dispersed phase drops. Soluble surfactants diffuse from the bulk phases to the interface, where a uniform distribution is maintained at equilibrium. Under an external flow field, surfactants are transported from the bulk to the interface by convection, in addition to diffusion. The relative rate of surfactant transport by convection to diffusion in the bulk is characterized by a Peclet number,  $Pe = Ga_0^2/D$ , where G is a measure of the shear rate of the ambient flow,  $a_0$  is the radius of the spherical drop, and D is the diffusion coefficient of the surfactant in the bulk. Surfactant molecules very close to the interface undergo adsorption from the bulk to the interface. Similarly, an adsorbed surfactant molecule can desorb from the interface to the bulk. Thus, surfactant exchange between the bulk and the interface is a reversible adsorption-desorption, or a sorption process $^{63,65}$ . The adsorbed surfactants get redistributed along the interface due to convection by the imposed flow, which gives rise to a nonuniform distribution of surfactants, leading to Marangoni stresses. This generates a Marangoni flow, which, in conjunction with diffusion of surfactants along the interface, acts to reestablish a uniform surfactant distribution. The relative rate of convection to diffusion of surfactants along

the interface is measured in terms of a surface Peclet number,  $Pe_s = Ga_0^2/D_s$ , where  $D_s$  is the diffusion coefficient of the surfactant along the interface. There have been a number of studies investigating the role of surfactants in emulsion rheology. Oldroyd<sup>110</sup> accounted for the interfacial rheology, considering a Boussinesq-Scriven interface, to derive an expression for the effective shear viscosity of a dilute emulsion akin to equations (4.1) and (4.2). Palierne<sup>111</sup> determined the linear viscoelastic modulus of emulsions of viscoelastic drops in a viscoelastic medium, accounting for interfacial rheology. Although the transport of surfactants was ignored in both these studies, the interfacial rheology, characterized by surface shear and dilatational viscosities, was supposed to arise from the presence of surface active species at the interface. The effect of insoluble surfactants and slight shape deformations of drops on emulsion rheology has been the focus of several theoretical and computational studies<sup>112–116</sup>. A central conclusion of these investigations is that when surfactant redistribution along the interface is significant, the emulsion shows a shear thinning viscosity, and finite normal stress differences.

The solubility of surfactants, along with interfacial rheology, i.e. surface shear and dilatational viscosities, was taken into account by Danov<sup>117</sup>. In that work, an expression for the effective shear viscosity of a dilute emulsion of spherical drops was derived and it was concluded that when the deviation from equilibrium is small, the emulsion behaves as a Newtonian fluid, with an effective shear viscosity greater than  $\mu_T$  (4.2), and less than  $\mu_E$  (4.1). However, that study considered the transport of surfactants from the bulk to the interface by diffusion alone, and assumed the kinetics of surfactant adsorption to be much faster compared to the flux due to diffusion at the interface. The effects of bulk convection and kinetic exchange of surfactants at the interface were not considered. Further, when surfactants are present in the drop phase, their adsorption to the interface may significantly reduce the equilibrium bulk concentration, an effect known as depletion<sup>118</sup>. Significant depletion will affect the interpretation of surface tension measurements in pendant drop apparatus<sup>119,120</sup>, and results in dramatic surface tension minima in multiphase fluid systems involving finite volumes<sup>121,122</sup>. The impact of depletion on bulk rheology of an emulsion has not been considered in detail; it is a goal of this study to do so.

In this chapter, we calculate the effective viscosity of a dilute emulsion of drops containing a soluble surfactant. The drops are assumed to remain spherical, and the transport of surfactant by bulk convection is considered weak, i.e., Pe is small. This holds true for millimeter size drops subjected to small shear rates  $\approx \mathcal{O}(10^{-3})s^{-1}$ . The surfactant is soluble only in the drop phase, and does not partition to the medium. Surfactant exchange between the drop and the interface is assumed to take place in a mixed diffusion-sorption controlled regime. The solution of the concentration and velocity fields is obtained as a regular perturbation expansion about the bulk Peclet number, upto  $\mathcal{O}(Pe)$ . We demonstrate that the transport and kinetics of surfactant adsorption, and surfactant depletion from the drop, can significantly affect the viscosity of the emulsion. At certain regimes we predict an effective viscosity greater than Einstein's result for rigid spheres.

### 4.2 Soluble surfactant in drops

#### 4.2.1 Problem setup

We consider an emulsion that is sufficiently dilute so that interaction between drops can be ignored; and so we only need to consider an isolated spherical drop of a Newtonian fluid with viscosity  $\hat{\mu}$  in another Newtonian fluid with viscosity  $\mu$ , subjected to a linear creeping flow, characterized by a shear rate

G. The radius of the drop is  $a_0$ , and the interfacial tension in the absence of surfactants is  $\gamma_0$ . The drop is loaded with surfactant molecules, with an initial bulk concentration  $C_i$ . The maximum packing surface concentration of the surfactant at the interface is  $\Gamma_{\infty}$ . The densities of the drop,  $\hat{\rho}$ , and the medium,  $\rho$ , are assumed equal. Figure 4.1 shows a schematic diagram of the problem, where the drop is subjected to a simple shear flow. We assume that the drops are neutrally buoyant, so the center of the drop is taken to be the origin of the coordinate system. We first formulate the problem in a dimensionless form, choosing  $a_0$  as the length scale,  $Ga_0$  as the velocity scale,  $\mu G$  as the scale for stresses,  $C_i$  as the scale for bulk concentration,  $\Gamma_{\infty}$  as the scale for interfacial concentration, and  $\gamma_0$  as the scale for interfacial tension. Henceforth, a superscript '\*' denotes a dimensional variable, and a lack of the superscript denotes a physical parameter, scale, dimensionless group, or the dimensionless version of a dimensional variable. We assume inertial effects to be negligible, i.e., the Reynolds numbers in the drop  $(Re = \hat{\rho}Ga_0^2/\hat{\mu})$  and the medium  $(Re = \rho Ga_0^2/\mu)$  are assumed to be very small. Further, we assume the drops to remain spherical under the imposed flow, i.e., the capillary number,  $Ca = \mu Ga_0 / \gamma_0 \ll \mathcal{O}(1)$ . These assumptions are reasonable for small applied shear rates and drops of small size. For example, a drop of water with radius  $100\,\mu m$  in  $500\,cSt$  silicone oil, subjected to a shear rate of  $10^{-3}\,s^{-1}$  will have  $\hat{Re} = 10^{-5}, Re \sim 10^{-6}, \text{ and } Ca \sim 10^{-6}.$  We examine the steady state solution of the problem.

#### Surfactant transport

The surfactant molecules inside the drop are transported to the interface by diffusion, as well as by convection due to the ambient flow. The surfactant transport is governed by the convection-diffusion equation, which in dimen-


Figure 4.1: Schematic of the drop with soluble surfactant subjected to a simple shear flow.

sionless form reads,

$$Pe \, \boldsymbol{\nabla} \boldsymbol{\cdot} \, (\hat{\boldsymbol{u}}C) = \nabla^2 C, \tag{4.3}$$

where  $\hat{\boldsymbol{u}}$  is the dimensionless velocity in the drop, C is the dimensionless concentration in the drop, and  $Pe = Ga_0^2/D$  is the bulk Peclet number, D being the diffusion coefficient of the surfactant in the drop. Surfactant molecules in the fluid film immediately next to the interface, or the sublayer, adsorb to the interface; and adsorbed surfactant molecules can desorb from the interface back to the drop. The surfactant concentration in the sublayer is controlled by diffusion from the drop, and this diffusion flux is given by  $j_d^* = -D\hat{\boldsymbol{n}} \cdot \nabla^* C_s^*$ , where  $\hat{\boldsymbol{n}}$  is the unit normal vector pointing out of the interface, and  $C_s^*$  is the sublayer surfactant concentration. Assuming that the surfactant molecules form a monolayer at the interface, the adsorption-desorption flux, or the sorption flux, follows the kinetic expression  $j_s^* = \beta C_s^*(\Gamma_{\infty} - \Gamma^*) - \alpha \Gamma^*$ , where  $\beta$ and  $\alpha$  denote the kinetic rate constants of adsorption and desorption, respectively, and  $\Gamma^*$  is the surfactant concentration at the interface<sup>65</sup>. At equilibrium  $j_s^* = 0$ , and the expression for the sorption flux reduces to the Langmuir adsorption isotherm,

$$\Gamma = \frac{kC_s}{1 + kC_s},\tag{4.4}$$

where  $\Gamma = \Gamma^*/\Gamma_{\infty}$  is the dimensionless surfactant concentration at the interface,  $C_s = C_s^*/C_i$  is the dimensionless sublayer surfactant concentration, and

#### CHAPTER 4.

 $k = \frac{\beta C_i}{\alpha}$  is the ratio of the desorption time scale  $(1/\alpha)$  to the adsorption time scale  $(1/\beta C_i)$ . Here, we consider the case where the surfactant exchange between the bulk and the interface is controlled both by diffusion and sorption, i.e.,  $j_d^* = j_s^*$  at the interface, which in dimensionless form gives,

$$-\hat{\boldsymbol{n}} \cdot \boldsymbol{\nabla} C = h Da\{C_s(1-\Gamma) - k^{-1}\Gamma\},\tag{4.5}$$

where  $Da = \frac{\beta C_i a_0^2}{D}$  is a Damkohler number, which is the ratio of the bulk diffusion time scale to the adsorption time scale, and  $h = \frac{\Gamma_{\infty}}{C_i a_0}$  is a dimensionless depletion depth, which is a measure of the thickness of a layer adjacent to the interface over which significant depletion of surfactant takes place. Alternately,  $h = \Gamma_{\infty} A^*/3C_i V^*$ , where  $A^*$ , and  $V^*$  are the area and volume of the spherical drop, respectively. Thus, h can also be thought of as the ratio of the minimum concentration of surfactant in the bulk required to populate the interface at maximum packing to the initial concentration of surfactant in the drop. This quantity is analogous to the parameter  $\zeta$  in Alvarez *et al.*<sup>118</sup>, and gives a measure of the extent of depletion.

At the interface, the adsorbed surfactant molecules also undergo transport by convection and diffusion, and this is governed by the interfacial transport equation<sup>65,123</sup>, which reads

$$\boldsymbol{\nabla}_{\boldsymbol{s}}^{\ast} \cdot (\boldsymbol{u}_{\boldsymbol{s}}^{\ast} \Gamma^{\ast}) - D_{\boldsymbol{s}} \nabla_{\boldsymbol{s}}^{\ast 2} \Gamma^{\ast} = j_{n}^{\ast}, \qquad (4.6)$$

where  $u_s^*$  is the surface velocity,  $D_s$  is the surface diffusion coefficient, and  $j_n^*$  is the flux exchange term with the bulk. For a mixed diffusion-sorption controlled exchange,  $j_n^* = j_d^* = j_s^*$ . Thus, in dimensionless form, the interfacial transport equation reads,

$$Pe \nabla_{s} \cdot (\boldsymbol{u}_{s} \Gamma) - \frac{1}{D_{r}} \nabla_{s}^{2} \Gamma = -\frac{1}{h} \hat{\boldsymbol{n}} \cdot \boldsymbol{\nabla} C_{s}, \qquad (4.7)$$

where  $D_r = D/D_s$ . Finally, since the surfactant is confined in the drop phase, we must account for a mass balance of the surfactant. Assuming

that the interface is initially free of surfactant, the mass balance equation is  $\int_{V^*} C_i dV^* = \int_{V^*} C^* dV^* + \int_{A^*} \Gamma^* dA^*$ , which in dimensionless form is

$$\frac{4\pi}{3} = \int_{V} CdV + h \int_{A} \Gamma dA.$$
(4.8)

### Fluid flow

The fluid flow in the drop and the medium will satisfy the Stokes equations when inertial effects are negligible. The fluid motion in the drop satisfies

$$\nabla \cdot \hat{\boldsymbol{u}} = 0,$$

$$M \nabla^2 \hat{\boldsymbol{u}} - \nabla \hat{p} = 0,$$
(4.9)

and the fluid motion in the medium satisfies

$$\nabla \cdot \boldsymbol{u} = 0,$$

$$\nabla^2 \boldsymbol{u} - \nabla p = 0,$$
(4.10)

where,  $(\hat{\boldsymbol{u}}, \hat{p})$  and  $(\boldsymbol{u}, p)$  denote the dimensionless velocity and pressure in the drop, and in the medium, respectively. The velocity and pressure fields at the center of the drop are bounded. The velocity in the medium approaches the far field velocity of the ambient linear flow,  $\boldsymbol{u}_{\infty} = \boldsymbol{G} \cdot \boldsymbol{x}$  as  $\boldsymbol{x} \to \infty$ . Here,  $\boldsymbol{G}$  denotes the dimensionless velocity gradient tensor of the ambient flow, and  $\boldsymbol{x}$  denotes the position vector measured from the center of the drop. In addition to these boundary conditions, the following conditions must be satisfied at the interface of the drop,  $r = |\boldsymbol{x}| = 1$ ,

$$\hat{\boldsymbol{u}} \cdot \hat{\boldsymbol{n}} = \boldsymbol{u} \cdot \hat{\boldsymbol{n}} = 0, \qquad (4.11)$$

$$\hat{\boldsymbol{u}} = \boldsymbol{u}, \tag{4.12}$$

$$\{\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}-(\boldsymbol{\sigma}:\hat{\boldsymbol{n}}\hat{\boldsymbol{n}})\hat{\boldsymbol{n}}\}-\{\hat{\boldsymbol{\sigma}}\cdot\hat{\boldsymbol{n}}-(\hat{\boldsymbol{\sigma}}:\hat{\boldsymbol{n}}\hat{\boldsymbol{n}})\hat{\boldsymbol{n}}\}=-\frac{1}{Ca}\boldsymbol{\nabla}_{\boldsymbol{s}}\boldsymbol{\gamma},\qquad(4.13)$$

where (4.11) is the kinematic boundary condition for a stationary interface, (4.12) specifies the continuity of velocity at the interface, and (4.13) corresponds to the tangential stress balance at the interface. Here,  $\boldsymbol{\sigma} = -p\boldsymbol{I} +$  $(\nabla u + \nabla u^{\dagger})$ , and  $\hat{\sigma} = -\hat{p}I + M(\nabla \hat{u} + \nabla \hat{u}^{\dagger})$  denote the dimensionless stress tensor in the medium and the drop, respectively, and the superscript '†' denotes the transpose of a tensor. The tangential stress balance neglects interfacial rheology, i.e., the existence of an interfacial shear or dilatational viscosity, by assuming an inviscid interface. The interfacial tension,  $\gamma$ , is related to the surfactant concentration at the interface through an equation of state. Surfactant molecules have finite dimensions, hence there is an upper limit on the number of molecules that can be accommodated in a monolayer. This is accounted for in the von Szyskowski equation of state,  $\gamma = 1 + E \ln(1 - \Gamma),$  where  $E = \frac{RTT_{\infty}}{\gamma_0}$  is the elasticity number, which signifies the sensitivity of  $\gamma$  to the surfactant concentration at the interface. This equation of state neglects interactions between the adsorbed molecules at the interface. Substituting the von Szyskowski equation in (4.13) we get

$$\{\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}-(\boldsymbol{\sigma}:\hat{\boldsymbol{n}}\hat{\boldsymbol{n}})\hat{\boldsymbol{n}}\}-\{\hat{\boldsymbol{\sigma}}\cdot\hat{\boldsymbol{n}}-(\hat{\boldsymbol{\sigma}}:\hat{\boldsymbol{n}}\hat{\boldsymbol{n}})\hat{\boldsymbol{n}}\}=\frac{Ma}{1-\Gamma}\boldsymbol{\nabla}_{\boldsymbol{s}}\Gamma,\qquad(4.14)$$

where the Marangoni number,  $Ma = RT\Gamma_{\infty}/a_o\mu G$ , signifies the ratio of Marangoni stresses to viscous stresses, R is the universal gas constant, and T is the temperature. The Marangoni number can also be written as Ma = E/Ca. In assuming that  $Ca \ll \mathcal{O}(1)$ , we lose the freedom of satisfying the normal stress balance condition at the interface, which, under this assumption, simply states that the drop remains spherical<sup>124</sup>. Further, since the elasticity number  $\sim \mathcal{O}(0.1)^{65}$ , the Marangoni number  $\approx \mathcal{O}(Ca^{-1})$  and is  $\gg \mathcal{O}(1)$ .

## 4.3 Emulsion rheology

### 4.3.1 Regular perturbation expansions

The solution for the surfactant distribution in the bulk and along the interface can be obtained by solving (4.3) and (4.7), subject to (4.5) and (4.8); and that of the fluid flow in the drop and the medium can be obtained from (4.9) and (4.10), subject to (4.11), (4.12), (4.14), and the respective boundary conditions at the center of the drop and at the far field. The tangential stress balance equation, and the governing equations for surfactant transport are nonlinear. Moreover, the surfactant transport and fluid flow equations are coupled. To enable an analytical solution, we examine the case of weak bulk convection (small Pe), and proceed by taking regular perturbation expansions about the Peclet number, upto  $\mathcal{O}(Pe)$ . We expand any variable of interest, say  $\psi$ , as

$$\psi = \psi_0 + Pe \,\psi_1 + \mathcal{O}(Pe^2), \tag{4.15}$$

where  $\psi_0$  is the leading-order solution, or the equilibrium solution, and  $\psi_1$  is the first order departure from equilibrium. At leading order, the surfactant transport equations (4.3) and (4.7) are decoupled from the flow field. That is, the flow does not affect surfactant distribution. The equilibrium solutions for surfactant distribution in the bulk and along the interface are

$$C_0 = \frac{1}{2}(1 - 3h - k^{-1}) + \frac{1}{2}\sqrt{(1 - 3h - k^{-1})^2 + 4k^{-1}},$$
 (4.16)

$$\Gamma_0 = \frac{kC_0}{1+kC_0}.$$
(4.17)

These expressions match the solution of the depleted bulk concentration in a spherical drop at equilibrium by Alvarez and co-workers<sup>118</sup> (equation (2) of that paper). When a surfactant adsorbs from a phase of finite volume to the interface, there can be three scales for the concentration. The first is the initial

concentration of the surfactant in that phase,  $C_i$ , the second is the minimum bulk concentration needed to populate the interface at maximum packing,  $C_{min} = \Gamma_{\infty} A^*/V^*$ , and the third is the ratio of desorption to adsorption rate constants,  $C_{cr} = \alpha/\beta$ , which is a measure of the critical concentration in the bulk above which surfactant adsorption is significant. From these three concentration scales, Alvarez and co-workers<sup>118</sup> defined two independent parameters,  $\zeta = C_{min}/C_i$ , and  $f = C_{min}/C_{cr}$  to quantify the depletion of surfactants. The parameters h and k in the present work arise naturally after non dimensionalizing the governing equations, and are related to  $\zeta$  and f as,  $h = \zeta/3$ , and  $k = f/\zeta$ . Similar to Alvarez and co-workers<sup>118</sup>, we find that depletion can only be neglected for very small values of h (< 0.01), or for larger values of h, when k is small enough (k < 0.01), as shown in Figure 4.2. For any other combination of (h, k), the surfactant depletion is significant. Particularly, in the limits  $h \to \infty$  and  $k \to \infty$  the surfactant is severely depleted from the drop.

The leading-order surfactant distribution profile at the interface is uniform, thus there are no Marangoni stresses acting at the interface. At leadingorder, the solution for the flow field is equivalent to the flow around a spherical drop with no surfactants, which is<sup>124</sup>

$$\hat{\boldsymbol{u}}_{\boldsymbol{0}} = \boldsymbol{\Omega} \cdot \boldsymbol{x} + \left[\frac{5r^2}{2(M+1)} - \frac{3}{2(M+1)}\right] \boldsymbol{E} \cdot \boldsymbol{x} \\ - \frac{1}{(M+1)} (\boldsymbol{E} : \boldsymbol{x}\boldsymbol{x}) \boldsymbol{x}, \qquad (4.18)$$

$$\hat{p}_0 = \frac{21M}{2(M+1)} \boldsymbol{E} : \boldsymbol{x}\boldsymbol{x},$$
(4.19)

$$\boldsymbol{u_0} = \boldsymbol{G} \cdot \boldsymbol{x} - \frac{M}{(M+1)r^5} \boldsymbol{E} \cdot \boldsymbol{x} - \left[\frac{5M+2}{2(M+1)r^5} - \frac{5M}{2(M+1)r^7}\right] (\boldsymbol{E}:\boldsymbol{x}\boldsymbol{x})\boldsymbol{x}, \qquad (4.20)$$



Figure 4.2: Plot of the equilibrium bulk concentration of the surfactant in the drop as a function of the dimensionless groups characterizing depletion. The symbols correspond to real systems, with the  $\triangle$  corresponding to water drops with SDS in olive oil,  $\circ$  corresponding to water drops with  $C_{10}E_8$  in silicone oil,  $\Diamond$  corresponding to water drops with  $C_{12}E_8$  in silicone oil, and  $\Box$  corresponding to water drops with  $C_{14}E_8$  in silicone oil. The parameters quantifying these systems are listed in Table 4.1.

$$p_0 = -\frac{(5M+2)}{(M+1)r^5} \boldsymbol{E} : \boldsymbol{x}\boldsymbol{x}, \qquad (4.21)$$

where  $\boldsymbol{E} = \frac{1}{2}(\boldsymbol{G} + \boldsymbol{G}^{\dagger})$  is the rate of strain tensor, and  $\boldsymbol{\Omega} = \frac{1}{2}(\boldsymbol{G} - \boldsymbol{G}^{\dagger})$  is the vorticity tensor of the ambient flow.

At  $\mathcal{O}(Pe)$  the surfactant transport and flow field equations are coupled. The bulk surfactant transport equation is

$$\nabla^2 C_1 = \boldsymbol{\nabla} \cdot (\hat{\boldsymbol{u}}_0 C_0), \qquad (4.22)$$

and the interface surfactant transport equation is

$$\boldsymbol{\nabla}_{\boldsymbol{s}} \cdot (\boldsymbol{u}_{\boldsymbol{s},\boldsymbol{0}} \boldsymbol{\Gamma}_0) - \frac{1}{D_r} \boldsymbol{\nabla}_{\boldsymbol{s}}^2 \boldsymbol{\Gamma}_1 = -\frac{1}{h} \hat{\boldsymbol{n}} \cdot \boldsymbol{\nabla} C_1, \qquad (4.23)$$

with the interface condition  $-\hat{\boldsymbol{n}} \cdot \boldsymbol{\nabla} C_1 = h Da\{C_{s,1}(1-\Gamma_0) - \Gamma_1(C_{s,0}+k^{-1})\},\$ and the mass balance condition  $\int_V C_1 dV + \int_A \Gamma_1 dA = 0.$ 

The  $\mathcal{O}(Pe)$  flow inside and outside the drop satisfies the continuity and Stokes equations, with the kinematic condition and continuity of tangential velocity at the interface. The interfacial stress balance equation has a contribution from the Marangoni stresses due to the coupling of the flow and surfactant equations, which leads to a nonuniform distribution of surfactants at the interface. The balance is

$$\{\boldsymbol{\sigma}_{1} \cdot \hat{\boldsymbol{n}} - (\boldsymbol{\sigma}_{1} : \hat{\boldsymbol{n}} \hat{\boldsymbol{n}}) \hat{\boldsymbol{n}}\} - \{\hat{\boldsymbol{\sigma}}_{1} \cdot \hat{\boldsymbol{n}} - (\hat{\boldsymbol{\sigma}}_{1} : \hat{\boldsymbol{n}} \hat{\boldsymbol{n}}) \hat{\boldsymbol{n}}\} = Ma(1 + \Gamma_{0} + \Gamma_{0}^{2}) \boldsymbol{\nabla}_{s} \Gamma_{1}.$$
(4.24)

The first order corrections to the surfactant distribution are linearly coupled to the flow field; thus the  $\mathcal{O}(Pe)$  solution is

$$C_1 = A\left(\boldsymbol{E}:\boldsymbol{x}\boldsymbol{x}\right),\tag{4.25}$$

$$\Gamma_1 = B\left(\boldsymbol{E}: \hat{\boldsymbol{n}}\hat{\boldsymbol{n}}\right),\tag{4.26}$$

$$\hat{\boldsymbol{u}}_{1} = \left[\frac{5D_{1}}{21}r^{2} + D_{2}\right]\boldsymbol{E} \cdot \boldsymbol{x} - \frac{2D_{1}}{21}(\boldsymbol{E}:\boldsymbol{x}\boldsymbol{x})\boldsymbol{x}, \qquad (4.27)$$

$$\hat{p}_1 = D_1 M(\boldsymbol{E} : \boldsymbol{x} \boldsymbol{x}), \qquad (4.28)$$

$$\boldsymbol{u}_{1} = -\frac{2D_{4}}{5r^{5}}\boldsymbol{E} \cdot \boldsymbol{x} + \left[\frac{D_{3}}{2r^{5}} + \frac{D_{4}}{r^{7}}\right](\boldsymbol{E}:\boldsymbol{x}\boldsymbol{x})\boldsymbol{x}, \qquad (4.29)$$

$$p_1 = \frac{D_3}{r^5} (\boldsymbol{E} : \boldsymbol{x}\boldsymbol{x}). \tag{4.30}$$

The  $\mathcal{O}(Pe)$  contribution only involves the rate of strain tensor, and not the vorticity tensor; hence, to  $\mathcal{O}(Pe)$  the rotational part of the flow does not

affect surfactant distribution. This would not be true at higher orders; e.g. at  $\mathcal{O}(Pe^2)$  there would be contributions from terms bilinear in E and  $\Omega$ , which would generate normal stress differences in addition to an effective viscosity. The constants  $A, B, D_i$  depend on the parameters  $h, k, Da, D_r, Ma$  and M, and are listed in Appendix C.

### 4.3.2 Average emulsion stress

For a dilute emulsion of torque free drops, the average stress in the bulk, in dimensional form, is given by 125,126

$$\boldsymbol{\Sigma}^* = -p^* \boldsymbol{I} + 2\mu \boldsymbol{E}^* + \bar{n} \boldsymbol{S}^*, \qquad (4.31)$$

where the first two terms represent the average stress in the medium phase in the absence of drops, and the last term is the contibution of the drop phase to the average stress. Here,  $\bar{n}$  is the number density of the dispersed phase drops, and  $S^*$  is the stresslet on a single drop, which arises due to the inability of the drop phase to deform affinely with the suspending medium. The stresslet is

$$\boldsymbol{S}^* = \frac{1}{2} \int_A (\boldsymbol{x}^* \boldsymbol{\sigma}^* \cdot \hat{\boldsymbol{n}} + \boldsymbol{\sigma}^* \cdot \hat{\boldsymbol{n}} \, \boldsymbol{x}) dA - \mu \int_A (\boldsymbol{u}^*_s \hat{\boldsymbol{n}} + \hat{\boldsymbol{n}} \boldsymbol{u}^*_s) dA.$$
(4.32)

The stresslet can be expanded as a regular perturbation in Pe, and the leadingorder and  $\mathcal{O}(Pe)$  corrections can be calculated from the solution of the flow field, (4.18)-(4.21), and (4.27)-(4.30). The final results are

$$\boldsymbol{S_0^*} = \frac{4\pi a_0^3}{3} \left(\frac{5M+2}{M+1}\right) \mu \, \boldsymbol{E^*},\tag{4.33}$$

$$\boldsymbol{S}_{1}^{*} = \frac{4\pi a_{0}^{3}}{3} \frac{3\Gamma_{0}D_{r}Ma(1+\Gamma_{0}+\Gamma_{0}^{2})}{5(M+1)^{2}} \Big[ 1- \Big\{ 1 + \frac{3\{2+hDa(1-\Gamma_{0})\}}{DaD_{r}(C_{0}+k^{-1})} \Big\}^{-1} \Big] \mu \boldsymbol{E}^{*}.$$

$$(4.34)$$

### 4.3.3 Effective viscosity

The effective stress is

$$\Sigma^{*} = -p^{*}I + 2\mu \Big[ 1 + \frac{\phi}{2} \Big( \frac{5M+2}{M+1} \Big) + Pe\phi \frac{3\Gamma_{0}D_{r}Ma(1+\Gamma_{0}+\Gamma_{0}^{2})}{10(M+1)^{2}} \Big\{ 1 - \Big( 1 + \frac{3\{2+hDa(1-\Gamma_{0})\}}{DaD_{r}(C_{0}+k^{-1})} \Big)^{-1} \Big\} \Big] E^{*}, \qquad (4.35)$$

which is of a Newtonian form with an effective viscosity

$$\frac{\mu_{eff}}{\mu} = 1 + \frac{\phi}{2} \left( \frac{5M+2}{M+1} \right) + Pe\phi \frac{3\Gamma_0 D_r M a (1+\Gamma_0+\Gamma_0^2)}{10(M+1)^2} \left[ 1 - \left\{ 1 + \frac{3\{2+hDa(1-\Gamma_0)\}}{DaD_r(C_0+k^{-1})} \right\}^{-1} \right],$$
(4.36)

where  $\mu_{eff}$  is the effective viscosity of the emulsion, and the volume fraction  $\phi = \bar{n} \frac{4\pi a_0^3}{3}$ . We predict the emulsion to exhibit a Newtonian behavior to  $\mathcal{O}(Pe)$ . At equilibrium (Pe = 0), the flow does not couple with the transport of surfactants, and the distribution of surfactants at the interface is uniform. In this limit, we recover the result of Taylor (4.2). Due to weak convection, the surfactant distribution at the interface is no longer uniform. This generates Marangoni stresses, which is represented by the last term in (4.36), and results in an effective viscosity greater than Taylor's prediction,  $\mu_T$ . Importantly, while Pe is assumed small, it is not necessarily true that the  $\mathcal{O}(Pe\phi)$  correction will be smaller than the  $\mathcal{O}(\phi)$  correction since it depends on several other parameters.

The viscosity of the emulsion depends on  $h = \Gamma_{\infty}/C_i a_0$ ,  $k = \beta C_i/\alpha$ ,  $Da = \beta C_i a_0^2/D$ ,  $D_r = D/D_s$ ,  $Ma = RT\Gamma_{\infty}/a_0\mu G$  and  $M = \hat{\mu}/\mu$ . All these parameters, except the viscosity ratio, are interfacial parameters, of which, the rate constants of desorption and adsorption ( $\alpha$  and  $\beta$ ) and the surface diffusion coefficient ( $D_s$ ) are particularly difficult to measure. Consequently, experimental data quantifying these parameters is scarce, more so for surfactant adsorption to liquid-liquid systems as compared to air-liquid systems. The kinetic parameters ( $\alpha$  and  $\beta$ ), and the maximum packing concentration at the interface ( $\Gamma_{\infty}$ ) can be measured from pendant drop apparatus to quantify surfactant adsorption. In these equipments, the surfactant transport to the interface is usually diffusion limited, thus only the ratio  $\alpha/\beta$  is obtained by fitting the adsorption data to an isotherm. Alvarez and co-workers<sup>127</sup> investigated the transport of a series of nonionic  $C_i E_j$  surfactants dissolved in water, to a water-silicone oil interface. Some of the surfactants studied showed transport in the mixed diffusion-sorption regime, thus  $\alpha$  and  $\beta$  were individually measured. The surface diffusion coefficient is more difficult to measure, and is usually assumed to be the same as the bulk diffusion coefficient, D, or within an order of magnitude of  $D^{128}$ .

Table 4.1: List of transport parameters obtained from literature of surfactants at oil-water interfaces<sup>127,128</sup>, dimensionless parameters which quantify the effective viscosity of the emulsion, and the scaled effective viscosity of the emulsion.

	Drop: Water	Drop: Water	Drop: Water	Drop: Water
	Medium: Olive oil	Medium: Silicone oil	Medium: Silicone oil	Medium: Silicone oil
	Surfactant: SDS	Surfactant: $C_{10}E_8$	Surfactant: $C_{12}E_8$	Surfactant: $C_{14}E_8$
$C_i (\mu M)$	$4 \times 10^{3}$	600	50	5
$a_0 \ (\mu m)$	100	75	75	75
$\Gamma_{\infty} \ (\mu mol/m^2)$	1.94	2.25	2.25	2.25
$D(m^2/s)$	$5 \times 10^{-10}$	$3.7 \times 10^{-10}$	$3.8 \times 10^{-10}$	$3.9 \times 10^{-10}$
$\alpha (1/s)$	0.1	$2.5 \times 10^{-2}$	$6.86 \times 10^{-6}$	$2.54 \times 10^{-8}$
$\beta \ (m^3/mol \ s)$	$5.7 \times 10^{-2}$	50	22.1	9.4
h	4.85	50	600	$6 \times 10^{3}$
k	$2.3 \times 10^{-3}$	1.2	160	$1.85 \times 10^{3}$
Da	$4.5 \times 10^{-3}$	0.45	$1.64 \times 10^{-2}$	$7 \times 10^{-4}$
Ma	$2 \times 10^5$	$3.1 \times 10^5$	$3.1 \times 10^5$	$3.1 \times 10^5$
M	$1.2  imes 10^{-2}$	$2 \times 10^{-3}$	$2 \times 10^{-3}$	$2 \times 10^{-3}$
$\left(\frac{\mu_{eff}}{\mu}-1\right)/\phi$	1.98	5.67	1.38	1.23

The effect of depletion of surfactants on the emulsion viscosity can be studied by choosing different h and k. These parameters can be independently changed for the same surfactant-fluid system by changing the initial concentration of surfactant in the drop, or the radius of the drop. In practice,

the extent to which these parameters can be changed will be restricted by the requirement that  $C_i$  has to be smaller than the critical micellar concentration of the surfactant, and that  $a_0$  must be small enough such that  $Ca \ll \mathcal{O}(1)$ . Moreover it is not possible to study the effect of solely changing either of the parameters quantifying depletion without also changing Da. Thus, among the parameters (h, k, Da), one can be held constant, but changing either one of the other parameters changes the third. In other words, it is physically not possible to isolate and study the impact of any one of these three parameters on  $\mu_{eff}$ . Here, instead of mathematically varying the parameters in an arbitrary fashion, we choose four different actual surfactant-fluid systems, with different (h, k, Da) to study how the transport and kinetics of surfactant adsorption, and depletion of surfactants influence the effective viscosity. The systems chosen are: (i) water drops with sodium dodecyl sulphate (SDS) in olive oil; (ii) water drops with  $C_{10}E_8$  in silicone oil; (iii) water drops with  $C_{12}E_8$ in silicone oil; and (iv) water drops with  $C_{14}E_8$  in silicone oil, and are denoted by the triangle, circle, diamond and square symbols, respectively, in Figure 4.2, and the inset in Figure 4.3. Their transport parameters are taken from Dunér et al.<sup>128</sup>, and Alvarez et al.<sup>127</sup>, and are listed in Table 4.1, along with values of the dimensionless parameters quantifying the effective viscosity. For all the systems, the surface diffusion coefficient has been assumed to be the same as the bulk diffusion coefficient, i.e.,  $D_r = 1$ , and the convection in the bulk is considered weak ( $Pe \sim 0.01$ ). The last row of table 4.1 lists the scaled effective viscosity of the emulsion,  $\left(\frac{\mu_{eff}}{\mu}-1\right)/\phi$ . Surprisingly, the effective viscosity of the water- $C_{10}E_8$ -silicone oil system is greater than a suspension of rigid spheres, for which  $\left(\frac{\mu_E}{\mu} - 1\right)/\phi = 2.5$ .

The  $\mathcal{O}(Pe\phi)$  contribution to the effective viscosity originates due to Marangoni stresses, which depends on the viscosity ratio, M, among other parameters. Figure 4.3 shows the scaled effective viscosity of the emulsions as a function of M. In experiments, M can be varied by changing the oil phase, or by using different grades of the same oil, which keeps the chemical composition constant. Although changing M may change the other dimensionless groups, they have been assumed constant in Figure 4.3. We recover Einstein's result for highly viscous drops, i.e., when  $M \to \infty$ . For certain combinations of (h, k, Da), the viscosity of the emulsion of drops is greater than  $\mu_E$ . Interestingly, the effective viscosity of these systems is predicted to increase as the drop phase fluid becomes less viscous. Although insoluble surfactants have been reported to significantly affect the viscosity of dilute emulsions<sup>112–116</sup>, a viscosity greater than Einstein's has not been predicted before. This suggests that the observed effect is due to the solubility of the surfactant.



Figure 4.3: Scaled effective shear viscosity of a dilute emulsion as a function of the viscosity ratio. The symbols correspond to the systems quantified in Table 4.1, and shown in the inset. For all the systems,  $D_r = 1$  and Pe = 0.01. The solid line corresponds to the effective viscosity of a dilute suspension of rigid spheres, as predicted by Einstein<sup>108</sup>.

### 4.4 Discussion



Figure 4.4: Sketch of the drop containing soluble surfactants subjected to a simple shear flow, decomposed as a linear combination of pure rotation and an extensional flow. The solid arrows show the direction of the ambient flow around the drop, the dashed arrows show the weakening of the flow around the drop due to its inability to deform like a fluid element, and the dotted arrows show the direction of the Marangoni flow.

For any emulsion, or suspension, the suspended drops or particles are unable to deform affinely with the suspending fluid, owing to a viscosity difference and an interfacial tension. This causes an energy dissipation in the system, ultimately resulting in an effective viscosity greater than the solvent viscosity. A general linear flow can be decomposed as a combination of a rotational flow and an extensional flow. Figure 4.4 shows the sketch of this decomposition for a simple shear flow, where the axes of extension and compression of the extensional component are at an angle  $\varphi = \pi/4$ , and  $\varphi = 3\pi/4$ , respectively, to the direction of the imposed flow. The drop will rotate with the rotational component of the flow. The straining component of the flow tends to stretch the drop along the axes of extension, and work has to be done against the interfacial tension and viscous forces in order to achieve this. This results in a weakening of the ambient flow around the drop, and the dashed arrows in the extensional part of the flow in Figure 4.4 depicts the fact that the drop resists stretching with the ambient flow. When surfactant molecules start adsorbing to the interface, they are convected by the straining component of the flow, from the axis of compression to the axis of extension. At  $\mathcal{O}(Pe)$ , the rotational component of the flow does not affect the distribution of surfactant. The straining component creates a nonuniform distribution in the surfactant concentration at the interface, and generates a Marangoni flow from the extensional axis to the compressional axis to reestablish a uniform distribution. This flow is depicted by the dotted arrows in Figure 4.4, and further resists the straining component of the flow. Thus, more work needs to be done to stretch the drop when a there is a nonuniform surfactant distribution at the interface. Consequently, in the presence of convection, the effective viscosity of the emulsion is greater than Taylor's prediction for surfactant-free drops. This is akin to the larger drag force experienced by a rising bubble or a settling drop in the presence of surfactant. Here again, the ambient flow due to the motion of the bubble or drop creates a nonuniform distribution of surfactant at the interface, which generates a Marangoni flow in a direction opposite to the ambient flow. A strong enough Marangoni effect can arrest the motion of the dispersed phase  $^{124,129}$ .

We attribute the prediction of an effective viscosity greater than Einstein's result to large Marangoni stresses, which are proportional to the Marangoni number and the surface gradient in interfacial surfactant concentration. The Marangoni number for all the systems is large ~  $\mathcal{O}(10^5)$  (Table 4.1). Figure 4.5 shows the  $\mathcal{O}(Pe)$  correction to the interfacial surfactant concentration. The leading-order solution,  $\Gamma_0$  is uniform, hence, the Marangoni stresses will be proportional to the nonuniformity in the distribution of  $\Gamma_1$ . The largest gradient in surfactant distribution corresponds to the largest Marangoni stresses, and this is observed for the system which shows the largest effective viscosity.

In Figure 4.6, we show velocity vector plots of the flow field inside and



Figure 4.5: Perturbation to the interfacial concentration distribution at  $\mathcal{O}(Pe)$ . The solid line represents the water-SDS-olive oil system, the dashed line represents the water- $C_{10}E_8$ -silicone oil system, the dotted line represents the water- $C_{12}E_8$ -silicone oil system, and the dash-dot line represents the water- $C_{14}E_8$ -silicone oil system. The inset shows the straining component of the ambient flow.

outside a drop, and compare this to the flow field around a rigid sphere, under a simple shear flow. We choose two systems for the drop, one where the effective viscosity is less than Einstein's prediction (water- $C_{14}E_8$ -silicone oil), and another where the effective viscosity is greater than Einstein's prediction (water- $C_{10}E_8$ -silicone oil). The rigid sphere corresponds to Einstein's calculation. A rigid sphere satisfies the no slip condition at the interface, and its surface velocity is purely rotational. Drops which maintain a steady state under an imposed field will support a tangential velocity. For a system where  $\mu_{eff} < \mu_E$ , the flow field around the drop is weaker than the ambient flow at far field, but is stronger than that around a rigid sphere. The system with  $\mu_{eff} > \mu_E$  shows regions of recirculation around the drop, suggesting that the Marangoni flow in these systems is strong enough to reverse the flow in the vicinity of the drop. As a result, the flow around the drop is weaker than the flow field around a rigid sphere, which gives rise to an emulsion viscosity greater than that of a suspension of rigid spheres. From the  $\mathcal{O}(Pe)$  solution of the flow field, it follows that the Marangoni flow decreases with the viscosity of the drop as  $1/(\lambda + 1)^2$ . This will become zero in the limit  $\lambda \to \infty$ . Hence, the regions of recirculation become smaller as  $\lambda$  increases, and the flow field around the drop eventually approaches that around a rigid particle. This explains the increase in effective viscosity for these systems with a decrease in the viscosity of the drop phase fluid, as seen in Figure 4.3.

It is known that a dilute suspension of charged rigid spheres has an effective viscosity greater than Einstein's prediction, which is referred to as the "primary electroviscous effect" <sup>130,131</sup>. Charged particles in solution are surrounded a layer of counterions, called the Debye layer, which can be viewed as a deformable microstructre. Under a weak imposed flow, the Peclet number for transport of ions is small. There is a slight deviation from the equilibrium distribution of ions in the Debye layer. This generates Maxwell electric stresses at the interface, which contributes to the effective viscosity of the suspension. Moreover, the distorted Debye layer has a net charge, and the action of an asymmetric electric field on this net charge can give rise to an electroosmotic flow, which generates an extra stresslet, further increasing the effective viscosity of the suspension<sup>132</sup>. For a dilute solution of charged, spherical drops, Ohshima<sup>133</sup> estimated the effective viscosity of the emulsion under a weak shear flow. His calculations show that when the thickness of the Debye layer is comparable to, or greater than the size of the drop, it is possible to get an emulsion viscosity greater than  $\mu_E$ . More recently, for drops of weakly conducting fluids suspended in a weakly conducting medium, an effective viscosity greater than  $\mu_E$  was predicted for certain cases, under a combined action of



Figure 4.6: Velocity vector for the the flow field: (a) around a rigid sphere  $(\mu_{eff} = \mu_E)$ , (b) inside and outside a drop for a system with  $\mu_{eff} < \mu_E$  (e.g., water-C<sub>14</sub>E<sub>8</sub>-silicone oil), and (c) inside and outside a drop for a system with  $\mu_{eff} > \mu_E$  (e.g., water-C<sub>10</sub>E<sub>8</sub>-silicone oil) shown in the velocity-gradient plane.

an electric field and shear flow, in the absence of surfactants<sup>134</sup>. For soluble surfactants, the distribution of surfactants in the bulk and along the interface can be viewed as the microstructure. Analogous to the Debye layer around a charged particle, an imposed flow will create a nonuniform distribution of the surfactant, generating Marangoni stresses, and for certain cases this contribution can result in an effective viscosity greater than a suspension of rigid spheres. Any mechanism that reduces the nonuniformity in surfactant distribution at the interface will weaken the stresslet associated with the Marangoni flow, and reduce the effective viscosity. Figure 4.7 shows the effect of increas-

ing the surface diffusion coefficient by an order of magnitude ( $D_r = 0.1$ ) on the effective viscosity for the systems shown in Figure 4.3. Surfactants at the interface undergo stronger diffusion along the interface, reducing the gradients in interfacial surfactant concentration, and consequently, the induced Marangoni flow. All the systems have an effective viscosity lower than  $\mu_E$  due to stronger surfactant diffusion along the interface.



Figure 4.7: Scaled effective shear viscosity of a dilute emulsion as a function of the viscosity ratio. The symbols correspond to the systems quantified in Table 4.1, and shown in Figure 4.2. For all the systems,  $D_r = 0.1$  and Pe = 0.01. The solid line corresponds to the effective viscosity of a dilute suspension of rigid spheres, as predicted by Einstein<sup>108</sup>.

Our analysis is valid when the drops remain spherical, do not interact, and the imposed flow is weak. An experimental verification of this theory might be challenging because of these restrictions. Thus, natural extensions to this work are to consider the effects of shape deformation, drop interactions, and strong imposed flows (large Peclet number). For a dilute suspension of charged rigid spheres with thin Debye layers, Russel<sup>131</sup> obtained a shear thinning response for the emulsion as the Peclet number increases. Under stronger imposed flows, the rotational component of the flow will influence the microstructure, in addition to the straining component, and will result in a non-Newtonian response, including normal stress differences. The effective viscosity in the presence of soluble surfactants is shown to depend on the transport and kinetic parameters of surfactant adsorption to liquid-liquid interfaces, and many of these parameters are poorly characterized. Measurement of kinetic rate constants of adsorption and desorption are limited because surfactant transport in pendant drop based equipments is usually diffusion controlled. It has been suggested that microscale interfaces, or convection in the bulk phase fluid, can shift the transport mechanism for some systems to a mixed diffusion-sorption controlled regime, enabling an estimation of these parameters  $^{135,136}$ . The surface diffusion coefficient is more difficult to measure. The usual practice is to assume it to be the same as the bulk diffusion coefficient, however, experiments to verify this assumption, or to study how  $D_s$  changes with the physical properties of the system are lacking. Development of experimental techniques to measure surfactant transport parameters to liquid-liquid interfaces is imperative to understand the rheology of emulsions with soluble surfactants.

### 4.5 Conclusion

We calculated the effective viscosity of a dilute emulsion of spherical drops containing a soluble surfactant, accounting for weak bulk convection. When surfactants are dissolved in the drop phase, they may get severely depleted from the bulk, if the initial surfactant concentration, or the drop size is small. At certain regimes of surfactant transport and depletion, Marangoni stresses may be large enough to generate regions of recirculation around the drops, resulting in an effective viscosity greater than Einstein's prediction for the

# Chapter 5

# Electric fields enable tunable surfactant transport to microscale fluid interfaces

# 5.1 Introduction

Electric fields act across fluid-fluid interfaces in electrocoalescence<sup>4,137</sup>, inkjet printing<sup>138,139</sup>, electroemulsification<sup>5,6,140</sup>, and microfluidic devices<sup>13–16</sup>. These systems typically consist of drops of one fluid dispersed in another, with surfactants adsorbing from the bulk phases to the interface. Electric fields give rise to stresses at the interface. Depending on the strength of the field, the interface may attain a deformed steady shape, or undergo an instability to form smaller drops. Interface deformation, and mechanisms of instability for systems of pure fluids, i.e., without added surfactant, has been well characterized<sup>23,24,26,32–37,73</sup>. The limited existing work on the deformation of surfactant-laden interfaces under electric fields is restricted to experiments and computations to predict drop deformation and breakup<sup>38–41,47,141</sup>. An inherent assumption in the computations is that the surfactant is insoluble; therefore, the effect of electric field on surfactant transport from bulk to the interface is not accounted for.

Surfactant transport from bulk to a fluid-fluid interface in the absence of electric field follows two transport processes<sup>43,44</sup>. Bulk surfactant diffuses to the interface (diffusion), and surfactant near the interface undergoes ad/desorption to/from from the interface (kinetic). The transport is known to be a function of bulk concentration, isotherm, local convection and interface geometry<sup>45,135,136,142–145</sup>. However, the impact of electric fields has not been determined. For oil-water interfaces, the electric field acts almost solely in the oil phase because the electrical conductivity of deionized water is nearly  $\mathcal{O}(10^6)$ larger than most oils. Surfactants are frequently added to oils and non-polar liquids in several applications. For example, OLOA 11000, a poly-isobutylene succinimide surfactant, is added to motor oil to prevent soot formation in internal combustion engines, disperse pigments in oils for use in electrophoretic displays, and even to prevent sparking during pumping of oils<sup>96,146,147</sup>. The addition of surfactants to oils has been observed to increase the electrical conductivity, both below and above the critical micellar concentration (CMC), even when the surfactant is considered nonionic  $^{96,148}$ . It is hypothesized that below the CMC surfactant molecules form complexes with ionic impurities in oil, which acquire charge by disproportionation<sup>148</sup>. An electric field will exert a force on these charged species, and could influence their bulk transport. Thus, the first step to accurately predict the deformation and breakup of surfactantladen interfaces under electric fields is to determine whether bulk surfactant transport couples with electric fields.

In this chapter, we present the first experiments to quantify the transport of oil-soluble surfactants to oil-water interfaces using a microscale capillary tensiometer platform, under a D.C. electric field. Dynamic interfacial tension was measured under different electric field strengths to determine the rate of surfactant transport to the interface. We show that for a system whose electrical conductivity increases on addition of surfactant, the transport is enhanced under electric fields. The rate of surfactant transport can be manipulated by tuning the strength of the electric field. On the contrary, a system whose electrical conductivity is unaffected by surfactant addition does not show any coupling of surfactant transport with electric field.

### 5.2 Materials and methods

The surfactants chosen were a poly-isobutylene succinimide surfactant, commercially known as OLOA 11000, donated by Chevron Oronite (San Ramon, CA, USA), and a polyethylene-polypropylene block copolymer, Pluronic L64, purchased from BASF. The surfactants were reported to have a molecular weight of 950 and 2900 g/mol, respectively. Stock solutions of 0.62 mM OLOA was prepared in Isopar-M, an alkane mixture purchased from Exxon Mobil, and 3.71 mM Pluronic was prepared in 100 cSt silicone oil, purchased from Gelest, Inc. The stock solutions were diluted to different concentrations for the experiments. Deionized water was taken from a Barnstead UV Ultrapure II purification system (resistivity of 18.2 M $\Omega$  cm).

The experimental setup is an electrified version of the microtensiometer platform, which was developed by Alvarez *et al.*<sup>145</sup>. The schematic is shown in Figure 5.1, with gravity pointing into the plane of the paper. Surfactant solution is filled in a cell of rectangular cross-section (35 mm ×25 mm), 3D printed using an acrylic material. Two electrodes are attached to opposite walls of the cell, 25 mm apart. Voltages in the range 0.1 - 2 kV were applied using a voltage source, setting electric fields ~ 0.04-0.8 kV/cm across the cell. The electrodes have a hole of diameter 6 mm drilled through them. A glass capillary containing deionized water is inserted through one of the walls of the cell, and one electrode. All capillaries used were pulled using a micropipette puller to diameters ~  $70 - 80 \ \mu$ m. The capillary is connected to a differential pressure transducer, with the other end connected to the opposite wall of the cell. The other two walls have glass windows to enable viewing of the interface, which is imaged using a camera attached to a Nikon microscope objective lens (20 X), and a radius fitted using a Labview routine. The capillary is inserted 6 mm away from the wall near the camera. COMSOL simulations predict the electric field lines to be unaffected by the wall when the gap between the wall and the capillary is more than twenty capillary radii. This chosen distance ensures that the capillary is within the field of view of the microscope objective, and field lines are not affected by the cell wall.



Figure 5.1: Schematic of the experimental setup. Top left inset shows COM-SOL simulations of electric field lines around a capillary of diameter 70  $\mu$ m.

Surfactant transport is quantified by the dynamic interfacial tension,  $\gamma$ , of the interface. This is obtained from the instantaneous measurement of

the radius of curvature of the hemispherical interface,  $R^*$ , and the pressure jump across the interface,  $\Delta P^*$ , using the Young-Laplace equation,  $\gamma = \Delta P^* \times R^*/2$ . The interface is maintained at a constant pressure head, and the change in interfacial tension is primarily accounted for by the change in radius of curvature of the interface. Under electric fields, the Laplace equation will have an additional contribution from electric (Maxwell) stresses acting at the interface, which scale as  $\epsilon_o E_{\infty}^{*2}$ , where  $\epsilon_o$  is the permittivity of the oil, and  $E_{\infty}^*$ is the field strength. The scaled normal stress balance equation at the interface assumes the form  $\Delta P = 2/R - Ca_E \Delta \tau_E$ , where  $Ca_E = R\epsilon_o E_{\infty}^{*2}/\gamma$  is the electric capillary number, and  $\Delta \tau_E$  is the dimensionless normal electric stress jump across the interface. For all field strengths and interface radii,  $Ca_E < \mathcal{O}(10^{-4})$ . Thus, electric stresses were ignored while calculating the dynamic interfacial tension. The low  $Ca_E$  also ensured that the interface remained hemispherical at all field strengths studied.

## 5.3 Results and discussion

The principle of the instrument has been previously used to characterize transport of surfactants from water to air-water<sup>136,145</sup>, and oil-water interfaces<sup>149,150</sup>, with the aqueous surfactant solution in the cell. Here, we have the oil-soluble surfactant in the cell, and water in the capillary; and quantify surfactant transport from the oil phase to the oil-water interface. The interfacial tension of pure Isopar-water was measured to be  $52.5 \pm 0.3$ , which is typical of alkanewater interfaces<sup>149</sup>, and that of silicone oil-water was  $40.3 \pm 0.4$  mN/m, in agreement with reported values<sup>127</sup>. Under an applied electric field, the interfacial tension was not observed to change beyond the error of the instrument (1 mN/m), for field strengths used in this study.

The transport and adsorption of OLOA in Isopar was measured to the

Isopar-water interface at two different surfactant concentrations (4  $\mu$ M and 10  $\mu$ M), under different electric field strengths. A new interface was formed by subjecting the drop phase in the capillary to a high pressure head, using a solenoid valve. For a newly formed interface, the interfacial tension starts decreasing from the clean interfacial tension value, and relaxes to a steady state of  $26.2 \pm 0.3$  mN/m for the 4  $\mu$ M system, and  $22.9 \pm 0.3$  mN/m for the 10  $\mu$ M system. The system is deduced to reach steady state when the interfacial tension does not change by more than 1 mN/m for at least 1000 The dynamic interfacial tension of the 4  $\mu$ M system is shown in Figure s. 5.2(a). For the experiments, data was collected at each millisecond; however, for clarity, we show fifty data points spaced equally on a logarithmic scale in the figure. The inset shows the dynamic interfacial tension for the last 1000 s under each electric field, with a shifted time axis, on a linear scale. Surfactant transport is known to depend on the radius of curvature of the interface $^{145}$ . In all the experiments, the pressure head was held constant at the same value, ensuring the initial radius of curvature for all the interfaces differed by  $< 5 \ \mu m$ . It follows that the time to reach steady state decreases with increasing values of the electric field. Under a field of 0.4 kV/cm, the system reaches steady state nearly four times faster than under no applied field. The effect is more prominent at lower values of the electric field. Dynamic interfacial tension curves for the 0.2 and 0.4 kV/cm nearly overlap with each other, having slightly faster dynamics under 0.4 kV/cm. All the curves reach the same steady state interfacial tension, indicated by the dashed line and depicted in the inset. This suggests that the electric field has negligible effect on the adsorption isotherm. The dynamic interfacial tension for 10  $\mu$ M OLOA showed a similar trend. Evidently, the transport of OLOA to the Isopar-water interface is enhanced under electric fields.

In contrast, the transport of Pluronic to the silicone oil-water interface



Figure 5.2: Dynamic interfacial tension for (a) 4  $\mu$ M OLOA 11000 in Isopar-M, and (b) 10  $\mu$ M Pluronic L64 in 100 cSt silicone oil. The dashed line represents the steady state interfacial tension. Inset: Dynamic interfacial tension for each system during the last 1000 s under each electric field. The time axis has been shifted so that all the curves fit in the same time range of 0 to 1000 s.

was not influenced by the electric field (Figure 5.2(b)). For a 10  $\mu$ M system, the interfacial tension relaxes from the clean value and approaches steady state. Even at the highest value of the field strength, the dynamic interfacial tension curve overlaps the curve obtained in the absence of a field. As shown in the inset, the interfacial tension did not completely relax to a steady state value, however the slope of the curves flatten out, suggesting that the system approaches steady state. Since the curves overlap each other throughout the experiment, we conclude that similar to the OLOA system, the steady state interfacial tension is unaltered by the electric field.

As a measure of the effect of electric field on surfactant transport, we plot the time required for the interfacial tension to relax from the clean value to a specific value,  $\gamma_t$ , for each system, as a function of the field strength. For OLOA in Isopar, we choose  $\gamma_t = 35$  mN/m, and for Pluronic in silicone oil,  $\gamma_t = 30 \text{ mN/m}$ . These values are chosen because they are roughly half the value of the interfacial tension of the pure oil-water interface and the steady state interfacial tension at the given surfactant concentration. For low bulk surfactant concentrations, as has been chosen in this study, a specific value of interfacial tension physically corresponds to the interface reaching a specific surfactant coverage. The result is shown in Figure 5.3. For the OLOA system, this time scale,  $t_{1/2}$  follows a power law scaling, with the exponents 0.41 and 0.52 for the 4  $\mu$ M and 10  $\mu$ M systems, respectively. The 10  $\mu$ M system reaches the same surfactant coverage faster than the 4  $\mu$ M system at all field strengths, in agreement with previous observations of faster diffusion from a more concentrated bulk solution to an interface<sup>145</sup>. The power law scaling with electric field is analogous to the effect of bulk phase convection on surfactant transport to fluid-fluid interfaces, rendered rigid due to large gradients in interfacial surfactant concentration<sup>136</sup>. Convection in the continuous phase reduces the effective boundary layer thickness for mass transport of the surfactant, thus, the time scale for the surfactant to diffuse from the bulk to the interface reduces. For Pluronic in silicone oil, the time scale does not change on the application of an electric field, as is shown by the dotted line.



Figure 5.3: Time required for the oil-water interface to reach an interfacial tension of 35 mN/m for OLOA 11000 in Isopar-M, and 30 mN/m for Pluronic L64 in silicone oil as a function of electric field. The dashed lines represent power law scalings for OLOA in Isopar-M. The horizontal dotted line establishes that the time scale is independent of field strength for Pluronic in silicone oil. The filled symbols denote the time scale under zero electric field. Inset: Electrical conductivity as a function of surfactant concentration. The arrow shows the CMC of OLOA 11000 in Isopar-L<sup>151</sup>. The dashed line shows the linear dependence of conductivity with concentration for OLOA in Isopar-M. The dotted horizontal line shows the conductivity of Pluronic in silicone oil is independent of surfactant concentration. The filled symbols denote the conductivity of pure oils, without externally added surfactant.

The observed phenomena can be explained from the measurement of the electrical conductivity of surfactant doped oils as a function of surfactant concentration, shown in the inset of Figure 5.3. The conductivity was measured using a nonaqueous conductivity probe, DT 700 (Dispersion Technology). For OLOA, the conductivity increases linearly, while for Pluronic, the conductivity

does not change with surfactant concentration. The CMC of OLOA 11000 in Isopar-L is reported to be around 140  $\mu$ M<sup>151</sup>, and is shown by the arrow in the inset. Assuming a similar CMC in Isopar-M, it follows that the conductivity of the oil increases both above and below the CMC, implying the presence of charged species even at concentrations below the CMC. Analogous to a previous study, we hypothesize that OLOA forms charged complexes with ionic impurities present in Isopar below the CMC<sup>148</sup>.

The surfactant complex experiences an electric force  $qE_{\infty}^*$ , where q is the charge of the complex. It moves with an electrophoretic velocity,  $U_E =$  $qE_{\infty}^{*}/6\pi\mu_{o}l$ , where  $\mu_{o}$  is the viscosity of the oil, and l is the characteristic linear dimension of the complex. Assuming, q is equal to the charge of one electron, and typical size of surfact ant molecules  $l\approx 5~{\rm nm}^{95},\, U_E\approx 5\times 10^{-3}\, 5\times 10^{-2}$  mm/s under the field strengths studied. For diffusion to spherical interfaces, the length scale for diffusion,  $h_s$ , depends on the radius of curvature of the interface, bulk concentration and isotherm<sup>135</sup>. We do not measure the equilibrium isotherm of OLOA at the Isopar-water interface, however, using typical parameter values of equilibrium surfactant coverage for surfactants at oil-water interfaces<sup>127</sup>, and the radii and bulk concentrations used in this study,  $h_s \approx 0.35 - 3.5$  mm. The time scale for the surfactant complex to migrate this distance under an electric field is  $t_E = h_s/U_E \approx 7 - 700$  s. The diffusion time scale is given by  $t_d = h_s^2/D$ , where D is the diffusion coefficient. For the dilute bulk surfactant concentrations chosen in this study ( $\leq 5 \times 10^{-4}$  wt %), we assume that the surfactant complexes do not interact with each other, and estimate D using the Stokes-Einstein equation,  $D = k_B T / 6\pi \mu_o l$ ,  $k_B$  and T being the Boltzmann constant and temperature, respectively<sup>152</sup>. Using this, we estimate  $t_d \approx 3.8 \times 10^3 - 3.8 \times 10^5$  s. An electric Pectlet number can be calculated as the ratio of the diffusion to electrophoretic time scale,  $Pe_E$  =  $qE_{\infty}^*h_s/k_BT$ . For the field strengths used in this study,  $Pe_E \sim 55 - 5500$ .

Even at the smallest field, electrophoretic migration is faster than diffusion. This manifests as an enhanced transport to the interface. Although a more rigorous analysis involving an investigation of the dependence of  $h_s$  on  $E_{\infty}^*$ , and measurement of charge on the complex is required to explain the power law coefficient, the migration of charged surfactant complexes under electric fields at time scales faster than the diffusion time qualitatively explains the results.

The Pluronic surfactant does not acquire charge in silicone oil, hence will not experience electrophoretic migration under an electric field. The conductivity difference between the silicone oil and water is huge: ~  $\mathcal{O}(10^6)$ . As a consequence, the tangential electric stresses at the interface is negligible, eliminating any electrohydrodynamic flow. Surfactant motion due to dielectrophoresis is nearly  $\mathcal{O}(10^{-3})$  slower than diffusion. Hence, the transport of Pluronic to silicone oil-water interface is not influenced by the applied field.

The surfactant transport can be precisely controlled by temporal variation of the field. This is demonstrated in Figure 5.4 for 4  $\mu$ M OLOA in Isopar-M. We performed an experiment which started under no external field. A field of 0.2 kV/cm was applied at 200 s, before steady state was reached. The transport dynamics changes at the instant the field is turned on, and the dynamic interfacial tension curve shifts from the curve obtained under zero field (for all times) to the curve obtained under 0.2 kV/cm (for all times). Another experiment was performed, which started under a field of 0.2 kV/cm, with the field switched off at 100 s. Again, the dynamics changes instantaneously with the field being turned off, and the curve shifts to the one obtained under zero field. Similar control and precision was observed in experiments performed at other field strengths, and for 10  $\mu$ M OLOA, confirming that this is a robust phenomena. Note that Figure 5.4 shows data 10 s after a new interface was formed; hence the curves do not start from the same value of interfacial

#### tension.



Figure 5.4: Dynamic interfacial tension for 4  $\mu$ M OLOA 11000 in Isopar-M at zero electric field ( $\circ$ ), 0.2 kV/cm ( $\diamond$ ), from zero field to 0.2 kV/cm at 200 s ( $\triangle$ ), and from 0.2 kV/cm to zero field at 100 s ( $\Box$ ). The arrows indicate the time when the field was switched off or on.

For all experiments where the field was turned on at some point before steady state, the time to shift from the curve under zero field to the curve under an applied field is around 100 s. This is comparable to the electrophoretic time,  $t_E$ , assuming  $h_s \sim 1$  mm, reaffirming that surfactant migration due to electrophoresis is likely responsible for this phenomena. The time scale to move from the curve under an applied field to a curve under zero field is significantly smaller than the diffusion time assuming  $h_s \approx 1$  mm.

Experiments performed with the direction of the electric field reversed showed the same effect as shown in Figures 5.2 and 5.4. This is expected because the interface is radially symmetric. Further, assuming disproportionation to be the charging mechanism, an equal number of positively and negatively charged surfactant complexes will be formed. Hence, the transport will be enhanced, regardless of the direction of the electric field.

The phenomena observed in this work would be difficult to capture in a pendant drop apparatus, which is traditionally used to measure surfactant transport to fluid-fluid interfaces. That technique requires millimeter size interfaces to accurately measure the dynamic interfacial tension. At such length scales  $Ca_E \approx 0.1$  resulting in significant deformation, or even electric field induced instability of the interface. This will significantly reduce the range of field strength that can be studied in such devices. Further, the time scale for adsorption to millimeter size interfaces is nearly an order of magnitude slower than to the microscale interfaces used here<sup>145</sup>; hence a significantly longer experiment would be needed to capture any effect. Although bulk phase convection has been observed to enhance surfactant transport<sup>136</sup> akin to electric fields, the "on-off" experiments shown in Figure 5.4 are more precise due to the instantaneous scheduling of the electric fields.

# 5.4 Conclusion

We have reported robust and novel experiments to demonstrate electric fields as a new parameter to precisely manipulate the rate of surfactant transport to microscale oil-water interfaces. This phenomena should be generic to oilsoluble surfactants which form charge carriers. The field enhanced transport could enable new tools for controlled electrocoalescence of drops in nonpolar media, or lab-on-chip methods for droplet manipulation in microfluidic devices.

# Chapter 6

# Dynamic interfacial tension measurement under electric fields allows detection of charge carriers in nonpolar liquids

# 6.1 Introduction

Control and characterization of the transport of surfactants to fluid-fluid interfaces is a key aspect to formulation design. In the absence of external fields, the transport and adsorption of a surfactant to an interface follows two simultaneous transport processes<sup>43–46</sup>. Surfactant molecules near the interface undergo adsorption and desorption from the bulk to the interface. This reduces the local surfactant concentration near the interface, establishing a concentration gradient across the bulk phases. Surfactant molecules diffuse from the bulk to the interface due to this concentration gradient. For an initially clean interface, the interfacial tension decreases on surfactant adsorption from the pure fluid-fluid interfacial tension, and relaxes to an equilibrium. The rate of surfactant transport is measured by the dynamic interfacial tension, and depends on the bulk concentration, isotherm, surfactant architecture and the geometry of the interface<sup>45,127,135,142,145</sup>. For a given system and geometry, it has been shown that the transport can be controlled using bulk convection<sup>136,143,144</sup>, demonstrating the utility of external fields.

In nonpolar liquids, like oils, the addition of surfactants has been shown to increase the electrical conductivity, even when the surfactant is nonionic<sup>95,148,153–157</sup>. This is explained by the formation and stabilization of charged species due to the amphiphilic nature of the surfactants. The origin of charge is thought to be inverse micelles, with water trapped in the core of the micelle and surrounded by the polar head groups of the surfactant. Two neutral micelles undergo random collisions due to Brownian motion and exchange an ion (usually identified as a proton), producing two oppositely charged micelles. This mechanism is known as disproportionation of charge<sup>95,148,151,156–159</sup>. Another proposed mechanism for the origin of charge is the steric stabilization of ionizable impurities in oils by surfactant aggregates<sup>154,160</sup>. If the added surfactant is ionic, charges may arise due to partial dissociation of the surfactant<sup>155,158</sup>. While the exact origin and constituents of charge is still debated, we have shown in the previous chapter that the transport of charge-forming surfactant aggregates in oil can be precisely manipulated using an external electric field.

A knowledge of the concentration of the charged species as a function of the added surfactant concentration is used to determine the charging mechanism in nonpolar media<sup>95</sup>. This is important in electrophoretic display technology<sup>157,161</sup>, neutralizing streaming currents to prevent sparks and explosions in oil transport<sup>147</sup>, and preventing soot formation in internal combustion engines<sup>162</sup>. Charge carrier concentration is usually determined by measuring the electrical conductivity of the nonpolar solvent as a function of surfactant concentration. The conductivity depends on the size and concentration of the charged species; thus, by estimating the size through dynamic light scattering
$(DLS)^{95,156}$ , the concentration of charge carriers can be estimated. However, most commercial surfactants are polydisperse, and DLS experiments detect aggregates of all sizes. Estimating the concentration from an average value of the aggregate size can lead to significant errors<sup>95</sup>. An alternate approach is to measure the Debye length using electrochemical spectroscopy techniques<sup>95,96</sup>, and relate it to the ionic strength of the solution, however interpretation of the results can become complicated due to adsorption of the charged species at electrodes<sup>95</sup>. Measurements of electrical conductivity is widely used to detect the presence of charged species in oils. Commercially available nonaqueous conductivity meters employed for this purpose can measure conductivity >  $10^{-11}$  S/m. This puts a lower limit to the surfactant concentrations that can be studied for the presence of charge apecies in oils, particularly at low surfactant concentrations can help understand charging in nonpolar media.

In the previous chapter, using a custom-built electrified capillary microtensiometer, we have shown that electric fields can be used to manipulate surfactant transport from bulk oil phases to oil-water interfaces, when the surfactant forms charged aggregates. In nonpolar fluids, the aggregation of surfactant molecules may occur over a range of surfactant concentrations, rather than at a distinct critical micellar concentration (CMC)<sup>156,163–166</sup>. The tendency of the formed aggregates to acquire charge depends on the solvent in which the surfactant is dispersed<sup>158</sup>, and size of the aggregates<sup>148,158</sup>, which in turn is a function of surfactant architecture<sup>167–169</sup>. In the previous chapter, we had dispersed two different surfactants in two different oils, and measured the interfacial tension as a function of time, i.e., the dynamic interfacial tension, to establish electric fields as a tool to manipulate surfactant transport in oils. In this chapter, we use surfactants having different structures and charging behavior in the same nonpolar medium, Isopar-M, to determine if dynamic interfacial tension measurements under electric fields can be used to distinguish surfactants having different charging mechanisms.

Here, two surfactants with different architecture are dispersed in an alkane mixture (Isopar-M), and the transport to an oil-water interface measured under different electric fields. The electrical conductivity of the oil is measured as a function of the surfactant concentration to determine the presence of charged species. The results are compared to the results of OLOA transport to the Isopar-water interface, discussed in the previous chapter. Next, the transport of an ionic surfactant from the aqueous phase to the oil-water interface is measured under electric fields. Finally, the effect of electric fields on the equilibrium interfacial tension is established. We provide further evidence that the coupling between surfactant transport and electric fields occurs due to electrophoresis of charged species. Measurement of the dynamic interfacial tension of oil-water interfaces is a sensitive tool to detect charged species in oils, particularly at low concentrations, and holds promise in understanding charging in nonpolar media.

## 6.2 Materials and methods

### 6.2.1 Materials

Isopar-M, an alkane mixture of dodecane and tridecane is obtained from Exxon Mobil (Houston, TX) and used as received. Two surfactants having a rake (R-M) and a double rake (DR-L) morphology are obtained from the Dow Chemical Company (Midland, MI) and dispersed in the oil phase. Both these surfactants are silicone polyether surfactants and have a polyethylene glycol (PEG) functionality. The DR-L surfactant has an additional functionality of a dodecyl group. The structure of the two surfactants is shown in Figure 6.1, along with the structure of a poly-isobutylene succinimde (OLOA 11000) surfactant for comparison to results of the previous chapter. The exact molecular weight of the two rake surfactants was not known, but reported by the supplier to be 2-5 kDa and 4-15 kDa for the R-M and DR-L surfactants, respectively. Hence, surfactant concentrations were reported as wt% in this work. Stock solutions of 0.32 wt% R-M and 0.25 wt% DR-L were prepared in Isopar-M, which were then diluted to different concentrations for the experiments. In addition, 100 cSt silicone oil was purchased from Gelest, Inc. For the aqueous phase, deionized (DI) water was taken from a Barnstead UV Ultrapure II purification system (resistivity of 18.2 M $\Omega$  cm). The ionic surfactant cetyltrimethylammonium bromide (CTAB) was purchased from Sigma-Aldrich (St. Louis, MO) at 99% purity, and dissolved in the aqueous phase at a concentration of  $3.64 \times 10^{-4}$  wt% (10  $\mu$ M), along with  $5.84 \times 10^{-2}$  wt% (10 mM) sodium chloride. The critical micellar concentration (CMC) was reported by the supplier to be  $3.28 - 3.64 \times 10^{-2}$  wt% (0.9 - 1 mM) in water, so the concentration used was below the CMC.

#### 6.2.2 Microtensiometer under electric fields

The experimental setup is an electrified version of the microtensiometer platform, which was developed by Alvarez *et al.*<sup>145</sup>. It is similar to the setup described in chapter 5, and is described in more detail here. The schematic of the equipment is shown in Figure 6.2, with gravity pointing into the plane of the paper. The device consists of a plastic cell with a rectangular cross-section (25 mm ×20 mm), machined out of Delrin <sup>®</sup>. The cell is 40 mm deep, and is filled with the oil phase fluid. There are two ports drilled on opposite walls of the cell. The ports are designed to be at the same height, although machining inaccuracy can result in a height difference of around 10  $\mu$ m. This translates







DR-L



Figure 6.1: Structure of (a) R-M (rake morphology), (b) DR-L (double rake morphology) and (c) OLOA 11000. The structures of the rake surfactants were provided by the supplier and that of OLOA 11000 was taken from Smith and Eastoe.<sup>157</sup>.

to a hydrostatic pressure difference of 0.08 Pa, which is nearly  $\mathcal{O}(10^{-5})$  smaller than the capillary pressure, hence is negligible. A glass capillary containing the aqueous phase fluid is inserted through one of the ports, and the other port is connected to one end of a differential pressure transducer (Omega Engineering, PX409-001DWU5V). The other end of the pressure transducer is connected to the end of the glass capillary using polyethylene tubing having an internal diameter of 1 mm. For this study, the glass capillaries were pulled to diameters between  $75-80 \ \mu m$ , using a PMP-102 micropipette puller (Micro Data Instrument, Inc.). Capillaries used for pulling were purchased from World Precision Instruments, Inc. (Sarasota, FL), and have an internal diameter of 0.75 mm, and an external diameter of 1 mm.



Figure 6.2: Schematic of the experimental setup. Gravity points into the plane of the paper. Top left inset shows COMSOL simulations of electric field lines around a capillary of diameter 70  $\mu$ m.

An interface between the oil and aqueous phase fluids is pinned at the tip of the capillary using a constant pressure head. This pressure head is generated using a water column attached to the capillary through the "normally open" port of a three-way solenoid valve, using polyethylene tubing (internal diameter of 1 mm). A high pressure head generated using a taller water column ( $\approx 35$  cm) is connected to the "normally closed" port of the solenoid valve. A new interface is generated by by pulsing the pressure head behind

the capillary phase fluid and ejecting a drop. The transverse walls have glass windows, which enable viewing the interface. The interface was imaged using a Labview subroutine, with a camera (Point Grey Grasshopper) attached to a Nikon microscope objective lens  $(20\times)$ . The captured image was analyzed *in situ* by fitting a circle to the interface. The National Instruments Vision toolbox was used for detecting the interface and fitting a radius.

The walls with ports for the capillary and the pressure transducer are also provided with slots for the insertion of stainless steel electrodes. Voltages in the range 0.1 - 0.8 kV were applied using a voltage source (Gamma High Voltage), setting electric fields  $\sim 0.05 - 0.4$  kV/cm across the cell, along the axis of the capillary. Switching the voltage on and off did not cause any fluctuations in the signals obtained from the pressure transducer, verifying that this range of voltage does not interfere with the electric signals of the pressure transducer. An electric field larger than 0.4 kV/cm caused the contact angle of the interface with the glass capillary to change due to  $electrowetting^{170}$ . Thus, fields larger than 0.4 kV/cm were not studied. COMSOL simulations were used to predict the distribution of electric field lines in the cell around the capillary. The simulations predict that electric field lines are not affected by the walls of the cell when the gap between the wall and capillary is more than 20 capillary radii. To ensure that the capillary is within the field of view of the camera, and the electric field lines are unaffected by the wall, it was placed at a distance of 6 mm (75 capillary radii) from the wall near the camera.

#### 6.2.3 Interfacial tension measurements

Surfactant transport is quantified by the dynamic interfacial tension,  $\gamma$ , of the interface. This is obtained from the instantaneous normal stress balance

across the interface, which can be written as

$$\Delta P^*(t) = \frac{2\gamma(t)}{R^*(t)} - \Delta \tau_E^*, \tag{6.1}$$

where,  $\Delta P^*$  is the Laplace pressure,  $R^*$  is the radius of curvature of the interface, and  $\Delta \tau_E^*$  is the jump in normal electric stresses at the interface, measured as the difference between electric stresses outside and inside the interface. The superscript, \*, denotes a dimensional quantity. The electric stresses scale as  $\varepsilon_o E_{\infty}^{*2}$ , where  $\varepsilon_o$  is the permittivity of the reservoir phase fluid, and  $E_{\infty}^*$  is the applied electric field; and is used to non-dimensionalize stresses. Scaling length with the capillary radius,  $R_c$ , and the Laplace pressure using the maximum capillary pressure ( $\gamma/R_c$ ), the non-dimensional form of the normal stress balance across the interface reduces to

$$\Delta P(t) = \frac{2}{R(t)} - Ca_E \Delta \tau_E, \qquad (6.2)$$

where  $Ca_E = \varepsilon_o R_c E_{\infty}^{*^2} / \gamma$  is the electric capillary number, which is a ratio of the electric stresses to the capillary pressure, and the terms without the superscript denote equivalent dimensionless quantities. Here, R and  $\Delta \tau_E \sim \mathcal{O}(1)$ , and for the electric field strengths used in this work,  $Ca_E < \mathcal{O}(10^{-4})$ . Thus, electric stresses were ignored from the normal stress balance, and the dynamic interfacial tension was calculated using the Young-Laplace equation,

$$\gamma(t) = \frac{1}{2}\Delta P^*(t) \times R^*(t).$$
(6.3)

The small value of the electric capillary number also ensures that the electric field does not deform the interface, or cause any interfacial instability<sup>22,37,39,42</sup>.

To verify that the scaling is correct and electric stresses can be ignored from the normal stress balance, the interfacial tension of oil-water interfaces with no added surfactant was measured under the highest electric field chosen in this study (0.4 kV/cm), and compared to the interfacial tension under no applied field. The result is shown in Figure 6.3, where the interfacial tension was measured for at least 1000 s. The interfacial tension of Isopar-DI water was measured to be  $52\pm0.6$  mN/m under no electric field, and  $51.7\pm0.3$  under 0.4 kV/cm; and that of 100 cSt silicone oil-DI water interface was measured to be  $39.9 \pm 0.4$  mN/m under no field, and  $39.5 \pm 0.4$  mN/m under 0.4 kV/cm. The measured values are in agreement with previously reported values<sup>127,149</sup>. For experiments under electric fields, a new interface was formed while the field was switched on, and the interfacial tension was measured using (6.3). Notably, the difference between the measured interfacial tension under zero field and the largest field applied is less than 1 mN/m, which is the error in interfacial tension measurement of the technique<sup>69,145</sup>. The sudden application of the electric field across an interface formed under zero field did not change the interfacial tension. This shows that the interfacial tension of Isopar-DI water and silicone oil-DI water interfaces with no added surfactant does not change under electric fields of up to 0.4 kV/cm. A similar observation was recently made for xylene-water interfaces under electric fields of up to 0.82 $kV/cm^{171}$ .

When surfactants are present, the interfacial tension of a new interface starts at the value of clean oil-water interfacial tension in the absence of surfactants, which is nearly 52 mN/m for an Isopar-DI water interface. As the surfactant adsorbs to the interface, the interfacial tension decreases and eventually relaxes to an equilibrium. Similar to the previous chapter, the interface was deduced to reach equilibrium when the interfacial tension does not change by more than 1 mN/m for a period of at least  $1000 \text{ s}^{69}$ . During the experiments, data was collected at every millisecond; however, for clarity, we first smooth the data using a piecewise cubic Hermite interpolating polynomial, and show 50 data points spaced equally on a logarithmic scale in all the figures. For a given surfactant concentration, the pressure head was held constant at the



Figure 6.3: Interfacial tension of Isopar-DI water and 100 cSt silicone oil-DI water under no field, and under 0.4 kV/cm.

same value, and changes in the interfacial tension occurred due to a decrease in the radius of curvature of the interface. This ensured that the initial condition for experiments conducted under different electric fields at a fixed surfactant concentration was the same.

### 6.3 Results and discussion

#### 6.3.1 Transport of oil-soluble surfactants

The transport of the rake (R-M) and double rake (DR-L) surfactants was measured to the Isopar-DI water interface, and is shown in Figure 6.4. For comparison, the transport of  $4.8 \times 10^{-4}$  wt% OLOA to the Isopar-DI water interface, which was shown in the previous chapter, is also shown. This data is reproduced from Figure 2(a) of that chapter, and corresponds to the dynamic interfacial tension of 4  $\mu$ M OLOA. At this concentration of OLOA, the interfacial tension of the Isopar-DI water interfaces relaxes to a steady state of  $26.3 \pm 0.3$  mN/m. The interface reaches steady state faster as the strength of the applied electric field increases. Under a field of 0.4 kV/cm, the steady state is reached nearly four times faster than under no applied field. The steady state interfacial tension is statistically the same under all applied fields, as indicated by the dashed line. The effect of electric field on surfactant transport is more prominent at smaller values of the electric field. The dynamic interfacial tension curves under 0.2 and 0.4 kV/cm nearly overlap each other, although slightly faster dynamics was observed under 0.4 kV/cm. Clearly, the transport of OLOA to the Isopar-water interface is enhanced under electric fields.

The dynamic interfacial tension of  $3.25 \times 10^{-4}$  wt% DR-L is shown in Figure 6.4(b) under different electric fields. For this system, the pressure head was initially maintained at 1500 Pa. A smaller pressure head generated a very flat interface  $(R^*(t)/R_c > 2)$  during the initial few minutes of the dynamics, which results in a large error in the measurement of the radius of curvature of the interface. The equilibrium interfacial tension at this concentration is  $17.5 \pm 0.6$  mN/m. In the figure, the dynamic interfacial tension data is shown until an interfacial tension of around 30 mN/m. At this value, the radius of curvature of the interface is very close to the radius of the capillary, and the interface gets ejected from the capillary tip if the pressure head is not reduced. Once this interfacial tension was reached, the pressure head was reduced to 750 Pa, and data was collected until the system relaxed to equilibrium. During the first 100 s, the transport of DR-L was only slightly enhanced by the electric field. Beyond this time, there is clearly an enhancement of the transport under electric fields. Under a field of 0.4 kV/cm, the interfacial tension reduced to 35 mN/m nearly three times faster than under no applied electric field. This observation is similar to the electric field-enhanced transport of OLOA 11000 and DR-L to the Isopar-DI water interface (Figure 6.4(a) and (b)).



Figure 6.4: Dynamic interfacial tension of (a)  $4.8 \times 10^{-4}$  wt% OLOA 11000, (b)  $3.25 \times 10^{-4}$  wt% DR-L and (c)  $1.6 \times 10^{-4}$  wt% R-M in Isopar-M. The dashed lines represent the equilibrium interfacial tension.

In contrast, the transport of R-M at a concentration of  $1.6 \times 10^{-4}$  wt% was not affected by the electric field (Figure 6.4(c)). The dynamic interfacial tension curves obtained under all electric fields nearly overlapped each other. The equilibrium interfacial tension at this concentration was measured to be  $34.3 \pm 0.8$  mN/m. The equilibrium was found to be nearly independent of the electric field, similar to measurements for the transport of OLOA 11000 and DR-L to the Isopar-DI water interface (Figure 6.4 (a) and (b)).

To further illustrate the effect of electric field on surfactant transport, the time taken for the interfacial tension to drop to half the interfacial tension of pure Isopar-DI water and the steady state interfacial tension at a given surfactant concentration,  $t_{1/2}$ , was plotted as a function of electric field. At the surfactant concentrations shown in Figure 6.4, this interfacial tension corresponds to a value of 35 mN/m for OLOA, 36.5 mN/m for DR-L and 43 mN/m for R-M. The result, shown in Figure 6.5, clearly demonstrates that electric fields enhance the transport of OLOA and DR-L to the Isopar-water interface, but does not affect the transport of R-M at  $1.6 \times 10^{-4}$  wt%. A one-way ANOVA test performed to establish the statistical significance verifies this conclusion. with the results shown in Table 6.1. For the data taken under an electric field, the time scale,  $t_{1/2}$  for OLOA transport shows a power-law scaling, with an exponent of 0.4, as shown by the dashed line in Fig 6.5. On the other hand, for DR-L,  $t_{1/2}$  decreases linearly as the applied field strength increases. An explanation for the observed trend in the time scale would require a detailed analysis of the adsorption isotherm, and is left as future work.

The electrical conductivity of Isopar-M as a function of the concentration of the two rake surfactants was measured, and is shown in Figure 6.6, along with the conductivity for OLOA in Isopar-M to compare to the previous chapter. The conductivity was measured using a nonaqueous conductivity probe (DT 700, Dispersion Technology). This instrument has a resolution of  $10^{-13}$ 



Figure 6.5: Time required for the interfacial tension to drop to half the interfacial tension of pure Isopar-DI water and the steady state interfacial tension. The filled symbols on the left show the time under no applied field. The dashed and dash-dotted lines are best fit lines to the data for OLOA and DR-L, respectively. The dotted horizontal line shows the time is independent of the applied field strength for R-M.

Table 6.1: Results of a one-way ANOVA test for the null hypothesis that the time to reach half the interfacial tension of pure Isopar-DI water and the steady state interfacial tension,  $t_{1/2}$ , does not change under an electric field.

Surfactant	F statistic	p value
OLOA 11000	33.39	$1 \times 10^{-8}$
DR-L	27.46	$3.6  imes 10^{-6}$
R-M	0.64	0.603

S/m; however considerable noise was observed in the data at low surfactant concentrations ( $< 10^{-3}$  wt%), where the measured average conductivity was  $< 10^{-11}$  S/m and the standard deviation was 25 - 50% the average value. The conductivity at these low concentrations is comparable to the measured conductivity of Isopar-M with no added surfactant, which is shown by the filled symbol on the left axis in Figure 6.6. At higher concentrations, the electrical

conductivity of Isopar-M increases linearly with the concentration of OLOA, both above and below the reported CMC in alkanes and alkane mixtures having a composition similar to Isopar-M  $(5 \times 10^{-3} - 1.68 \times 10^{-2} \text{ wt\%})^{151,159}$ ; and nearly as the square root of the concentration of DR-L. There is no significant increase in the conductivity with addition of R-M. The conductivity increases by factor of 2 at a concentration of around  $10^{-2} \text{ wt\%}$ , however, further addition of surfactant did not systematically increase the conductivity.



Figure 6.6: Electrical conductivity of Isopar-M as a function of concentration of added surfactant. Symbols denote experimental measurements, and the dashed lines show the trend in conductivity with surfactant concentration. The filled symbol on the left axis denotes the conductivity of Isopar-M with no added surfactant.

An increase in electrical conductivity with surfactant concentration is indicative of the presence of charged species, which is attributed to water-swollen inverse surfactant micelles, or ionic impurities in oils sterically stabilized by surfactants<sup>95,148,151,154,155,157–160</sup>. It has been suggested that in nonpolar liquids, a distinct CMC may not exist, and aggregation of surfactant molecules into micelles in nonpolar solvents may occur either at a distinct concentration, or gradually over a range of concentrations, depending on the polarity of the surfactant molecule<sup>163–166</sup>. A linear increase in conductivity with concentration can be explained by disproportionation of charge by the collision of two neutral aggregates - inverse micelles, or complexes of ionizable impurities with surfactant molecules<sup>95,148,151,157–160</sup>. An increase in conductivity as the square root of concentration is attributed to partial dissociation of ion pairs, and has been observed with dioctyl sodium sulfosuccinate (NaAOT) in hexadecane at concentrations below the CMC<sup>155</sup>. The structure of DR-L does not suggest any ionizable group. Further, conductivity measurements and preliminary experiments done with dynamic light scattering (DLS) did not reveal any distinct CMC. Hence, instead of determining the constituents of charges, we conclude that addition of both OLOA 11000 and DR-L to Isopar-M gives rise to charged species, most likely by different charging mechanisms. An electric field will act on these species and give rise to an electrophoretic transport, in addition to the diffusive transport of the surfactant from the bulk to the interface. This manifests as an enhanced transport, observed in the dynamic interfacial tension measurement for OLOA and DR-L (Figure 6.4 (a) and (b)). The difference in the observed scaling of  $t_{1/2}$  with  $E_{\infty}^{*}$  for these two surfactants could also be attributed to their different charging mechanisms in Isopar-M, as evidenced by the conductivity data (Figure 6.6).

Notably, the electrical conductivity of Isopar-M at the concentrations of the three surfactants studied in Figure 6.4 is not statistically different from each other, or from the conductivity of Isopar-M with no added surfactant. As such, a measurement of the conductivity alone at these lower concentrations would lead to a conclusion of the absence of charge carriers. The three surfactants, however, show a different response under an electric field. In particular, the field-enhanced transport of OLOA and DR-L are indicative of the presence of charged species which respond to the applied field. This demonstrates that at low surfactant concentrations, a measurement of the dynamic interfacial tension of oil-water interfaces under electric fields is a sensitive tool to detect the presence of charged species in oils.

The conductivity of Isopar-M increased by a factor of 2 with the addition of R-M at a concentration of around  $10^{-2}$  wt%. Although there is no significant increase in conductivity with further increase in the concentration. the dynamic interfacial tension for both R-M and DR-L was measured around this concentration to check for field-enhanced surfactant transport. The results are shown in Figure 6.7 (a) for  $1.3 \times 10^{-2}$  wt% DR-L and Figure 6.7 (b) for  $8 \times 10^{-3}$  wt% R-M. For both these systems, the interfacial tension was observed to relax to values < 10 mN/m. At these low interfacial tensions, the constant pressure head,  $\Delta P^*$  needs to be reduced to nearly 400 Pa, which is around four times the accuracy of the pressure transducer. This compromises the accuracy of the measured interfacial tension. Consequently, an equilibrium interfacial tension was not measured at these concentrations. Instead, the dynamics of surfactant transport was probed till the interfacial tension reduced to around 20 mN/m for the DR-L system, and 17 mN/m for the R-M surfactant. The transport of both surfactants at the higher concentration was faster for all fields when compared to experiments performed at a lower concentration (Figure 6.4). This is in agreement with previous observations of faster transport of surfactants from more concentrated bulk solutions, when the transport is in the diffusion limited regime  $^{127,135}$ . Further, even under no applied field, the interfacial tension relaxed to the measured limits relatively fast, at around 600 s for DR-L and 80 s for R-M. Given the narrow range in time for the decrease in interfacial tension, rather than measuring the transport over a range of different electric field strengths, experiments were performed which started under no applied field. A field of 0.2 kV/cm was then applied at 70 s for DR-L and 15 s for R-M, analogous to the experiments performed

with OLOA in Isopar-M in the previous chapter. For both the surfactants, the transport dynamics changed instantaneously with the application of the field. The dynamic interfacial tension curve shifted from the curve obtained under no field at all times to the curve obtained under 0.2 kV/cm at all times. Another experiment was performed where the measurement was started under 0.2 kV/cm, with the field being switched off at 50 s for DR-L, and 8 s for R-M. Again, for both surfactants, the dynamics changed at the instant the field was switched off, and the dynamic interfacial tension curve shifted from the one obtained under 0.2 kV/cm at all times to the one obtained under no field at all times. For both DR-L and R-M, an electric field enhanced the transport at these higher concentrations.

The enhancement in transport of the DR-L surfactant at the higher concentration is expected, given a similar observation at a lower concentration. It can be explained by the electrophoresis of charge carriers under electric fields, the presence of which was indicated by the increase in Isopar-M conductivity with addition of DR-L (Figure 6.6). On the contrary, the transport of R-M, which was not affected by electric fields at a lower concentration  $(1.6 \times 10^{-4})$ wt%), was influenced at  $8 \times 10^{-3}$  wt%. A field-enhanced transport for R-M was also observed at an even higher concentration of  $1.6 \times 10^{-2}$  wt%, but is not shown here. The conductivity of Isopar-M remained relatively constant with increasing concentration of R-M, until around  $10^{-2}$  wt%, where the conductivity almost doubled. This, coupled with the observation of a field-enhanced transport around a similar concentration suggests the presence of charged species, which most likely can be attributed to surfact and aggregates<sup>148,154,158</sup>. Although further addition of surfactant did not show a systematic increase in the conductivity, previous studies have shown that the aggregation of surfactants to micelles in nonpolar liquids can occur gradually over a range of concentrations, depending on the polarity of the surfactant<sup>163,166</sup>. The ten-



Figure 6.7: Dynamic interfacial tension of (a)  $1.3 \times 10^{-2}$  wt % DR-L and (b)  $8 \times 10^{-3}$  wt % R-M in Isopar-M, performed under no field ( $\circ$ ), 0.2 kV/cm ( $\diamond$ ), no field to 0.2 kV/cm ( $\triangle$ ) and 0.2 kV/cm to no field ( $\Box$ ). The arrows indicate the time when the field was switched on or off.

dency of surfactant aggregates to acquire charge and give rise to conductivity was shown to depend on the size of the aggregates<sup>148</sup>, which in turn depends on the surfactant architecture<sup>167–169</sup>. Thus, the formation of charge carriers, charging mechanism, and coupling of electric fields and surfactant transport in nonpolar liquids depends on the polarity and architecture of the surfactant molecule. The transport of surfactants to oil-water interfaces can be precisely manipulated using electric fields at these concentrations where the surfactant forms charged aggregates.

We reiterate that the measurement of solely the electrical conductivity of Isopar-M doped with R-M would not detect charge carriers, especially at a concentration of  $8 \times 10^{-3}$  wt% because the conductivity till this concentration is not statistically different from the conductivity of Isopar-M with no added surfactant. Measurements of the dynamic interfacial tension for these low conductivity systems is a more sensitive technique to ascertain the presence of charge carriers, and detect changes in charge carrier concentration with the addition of small amounts of surfactant. It is still unclear how the concentration of charge carriers, or the charging mechanism can be determined from the dynamic interfacial tension data or the observed scaling of  $t_{1/2}$  with  $E_{\infty}^*$ obtained from these experiments. Nevertheless, dynamic interfacial tension measurement under electric fields shows promise to understand charging in nonpolar media, particularly at low surfactant concentrations.

### 6.3.2 Transport of ionic surfactants in aqueous phase

Next, the transport of the cationic surfactant CTAB from the aqueous phase to the oil-water interface was studied under electric fields. A  $3.64 \times 10^{-4}$  wt% concentration of the surfactant was prepared in a solution of  $5.84 \times 10^{-2}$  wt% sodium chloride. The result is shown in Figure 6.8. The interfacial tension relaxes to an equilibrium of  $34.5 \pm 0.7$  mN/m, indicated by the dashed line. Evidently, the transport of the cationic CTAB does not depend on the electric

field. The electrical conductivity of deionized water is nearly  $\mathcal{O}(10^6)$  larger than Isopar-M. Adding salt further increases the conductivity. Due to the large difference in conductivity, the aqueous phase can be considered to be a conducting fluid. The electric field inside the aqueous phase scales as the ratio of conductivity of the oil to aqueous phase, and is nearly zero<sup>22</sup>. Thus, although cationic surface active species are present in the aqueous phase, there is no electric field to drive the charged species to the interface. As a result, the transport of surfactants from an aqueous phase to oil-water interfaces is not affected by an electric field. This further verifies that the enhancement in transport observed for oil-phase surfactants is caused by the electrophoretic motion of charge carriers.



Figure 6.8: Dynamic interfacial tension of  $3.64 \times 10^{-4}$  wt% CTAB in  $5.84 \times 10^{-2}$  wt% sodium chloride. The dashed line represents the equilibrium interfacial tension.

### 6.3.3 Equilibrium interfacial tension

Finally, the effect of electric field on the equilibrium interfacial tension at the Isopar-DI water interface was measured. The result is shown in Figure 6.9 for OLOA 11000, DR-L, R-M and CTAB at a given concentration for electric fields of up to 0.4 kV/cm. A one-way ANOVA test (Table 6.2) shows that the value of the F statistic is  $\mathcal{O}(1)$ , and the p value is > 0.05 for all four surfactants. Hence, it follows that the equilibrium interfacial tension does not change under an applied electric field of up to 0.4 kV/cm. Although a full adsorption isotherm was not measured, we conclude that the isotherm parameters do not change under electric fields.



Figure 6.9: Equilibrium interfacial tension of the surfactants plotted as a function of the electric field strength. The dashed line denotes the interfacial tension of an Isopar-DI water interface in the absence of added surfactant.

F statistic	p value
0.65	0.5823
2.17	0.1265
0.05	0 4697
0.95	0.4027
0.38	0.7
	F statistic 0.65 2.17 0.95 0.38

Table 6.2: Results of a one-way ANOVA test for the null hypothesis that the mean equilibrium interfacial tension does not change under electric field.

### 6.4 Conclusion

The transport of surfactants which form charged aggregates in nonpolar liquids is enhanced to oil-water interfaces under electric fields. The accelerated transport occurs due to the electrophoretic motion of the charged species under electric fields. The formation of charge carriers and the charging mechanism depends on the concentration, polarity and architecture of the surfactant molecules. Two surfactants with different architecture were dispersed in Isopar-M, and the transport was measured to an Isopar-water interface. The DR-L surfactant, having a double rake morphology showed a field-driven transport at both concentrations studied, analogous to the field-enhanced transport of OLOA reported in the previous chapter. The R-M surfactant, with a rake morphology showed a field-enhanced transport at the higher concentration studied, and a field-independent transport at the lower concentration. The transport of ionic surfactants in the aqueous phase was not influenced by an electric field. The electric field in the aqueous phase is nearly zero due to the large electrical conductivity of the aqueous phase compared to the oil phase. This further verifies that the field-enhanced transport for the oil-phase surfactants is due to electrophoresis of charged species. The equilibrium interfacial tension did not change on the application of an electric field, suggesting the surfactant adsorption isotherm is not a function of the electric field.

At low surfactant concentrations, the electrical conductivity of oils is very small. The sole measurement of the electrical conductivity could erroneously suggest the absence of charged species in the nonpolar phase. We show that at these low concentrations, measurement of the dynamic interfacial tension of an oil-water interface under electric fields is a sensitive tool to detect the presence of charge carriers, which would go unnoticed by conductivity measurements. Notably, surfactants with different charging mechanisms show a different dynamic response to the electric field. It remains to be determined how the concentration of charge carriers, or the specific charging mechanism can be determined from the dynamic interfacial tension data. Measuring the adsorption isotherm to obtain pertinent length scales for surfactant transport, and a rigorous analysis of the time scale to reach half the clean interfacial tension and equilibrium interfacial tension value might offer useful information. The charging of nonpolar phases at high surfactant concentrations, where electrical conductivity can be confidently measured is relatively well explored, but charging at low surfactant concentrations could potentially be understood through dynamic interfacial tension measurements under electric fields.

Electric fields also show promise as a robust tool to selectively manipulate surfactant transport to oil-water interfaces. For example, in a dispersion containing both DR-L and R-M, the transport of DR-L can be preferentially enhanced by switching on an electric field, provided the concentration of R-M is low. A careful molecular design of surfactant to control the range of concentrations where the surfactants form aggregates and acquire charge will enable precise and selective manipulation of the transport of oil-soluble surfactants in the oil phase. Hence, these fields could be employed to preferentially transport oil-soluble surfactants to oil-water interfaces in applications where surfactants from both the aqueous and oil phase are adsorbing to the interface. The application of electric fields to surfactants dispersed in oil provides us with an opportunity to precisely and selectively manipulate transport, and further understand charging in nonpolar media.

# Chapter 7

## Conclusions

We have quantified the response of liquid drops, and surfactant transport to interfaces, under electric fields. The response of the drops encompasses transient deformation and identifying the critical condition and mechanism of breakup; and quantifying surfactant transport entails measuring the dynamic interfacial tension. In chapter 2, we highlighted that surface charge convection reduces critical field strength for breakup, and changes the breakup mechanism of leaky dielectric drops from end-pinching to breakup via conical ends. In chapter 3, we demonstrated that fluctuations in the external electric field increases the average drop deformation, reduces the time for breakup, and broadens the transition from steady state to breakup. In chapter 4, we documented that small amounts of soluble surfactant added to a drop phase can greatly affect the viscosity of a dilute emulsion of such drops for certain regimes of surfactant transport and depletion. In chapter 5, we demonstrated that electric fields can be used to precisely manipulate the transport of oil-soluble surfactants to oil-water interfaces. In chapter 6, we established that the measurement of dynamic interfacial tension under electric fields is a sensitive technique to detect the presence of charged species in nonpolar phases, particularly at low surfactant concentrations.

### 7.1 Impact

To design a system and select operating conditions, an engineer needs to know the system response under different operating conditions, and understand the tools that can be used to manipulate the process. In our computations to predict the drop response under a uniform and random electric field, we have provided phase maps in the space of relevant dimensionless parameters for the final state of the drop. We explain the different modes of breakup and a transition in the breakup mechanism observed for weakly conducting drops. If the effect of surface charge convection is neglected while modeling these systems, the engineer might choose a certain operating condition expecting breakup via end-pinching, but end up with much smaller drops during the process, due to conic cusping. We demonstrate that fluctuations in the external field, caused by drop interactions or disturbances in operating conditions can result in bimodal states of drop deformation, and result in breakup at sub-critical fields. In electrocoalescers, the operator might decide to use a high, but sub-critical field strength to maximize drop collisions and separation efficiency. However, due to field fluctuations caused by interacting drops, one may end up with a more emulsified system instead of achieving coalescence and separation. The operating phase maps presented in this thesis will provide guidelines on the parameters that can be tuned to yield a desired drop response in devices.

The control of surfactant transport to interfaces is central to formulation design. We establish, using the electrified microtensiometer, electric fields as a new tool that can precisely and selectively transport surfactants at oil-water interfaces. For surfactants forming charged aggregates in the oil phase, turning an electric field on will accelerate the surfactant transport to an interface. This can be exploited to understand charging in nonpolar media. The electric field-induced enhancement in transport is more precise than using an external flow field because electric fields can be scheduled instantaneously. Moreover, the field-enhanced effect solely affects transport in oil phases. In systems where multiple surface active species are adsorbing to an interface from both an oil phase and the aqueous phase, electric fields can be used to control the composition of the interface. A surfactant-laden interface has a specific rheological response; thus, by controlling the species and amount of surfactant at an interface, we can engineer interfaces with a specific interfacial mechanics.

The work presented in this thesis is a significant step forward in understanding the electrohydrodynamics of surfactant-laden interfaces, and developing tools to manipulate surfactant transport to interfaces.

## 7.2 Future work

We have the skills and tools to further develop the subject of surfactant-laden interfaces under electric fields. The results in chapters 5 and 6 have shown that electrophoresis of charged, surface active aggregates results in an enhanced transport to interfaces. More specifically, in chapter 6, we have shown that the coupling of surfactant transport to electric fields depends on the surfactant architecture, and can be used to detect the presence of charge carriers in the oil phase. An accurate determination of the electrophoretic time scale  $(t_E = 6\pi h_s \mu_o l/q E_{\infty}^*)$  will help us understand better which surfactant or system feature needs to be altered to evoke a specific response. The first step to determine this is to measure the adsorption isotherm of surfactants, which enables calculation of the depletion depth,  $h_s$ . By choosing different surfactants and electric field strengths, we can obtain a range of  $t_E$ , and thus the electric Peclet number  $Pe_E$ , and analyze how this affects the coupling between electric fields and surfactant transport. Another means to change  $Pe_E$  is to control the charge of the surface-active species. Surface-active ionic liquids<sup>172,173</sup> hold promise as candidates for charged surfactants in oil phases. The charging mechanism for these surfactants are likely different from the surfactants used in this work. Hence, studying the transport of these surfactants will also elucidate how the charging mechanism influences surfactant transport under electric fields.

From a more applied perspective, the transport of multiple surfactants to an interface can be studied, where electric fields can be used to guide a desired surfactant preferentially to the interface. The results in chapter 6 demonstrate that electric fields selectively enhance the transport of surfactants in the oil phase, but do not influence the transport of even ionic surfactants in the aqueous phase. In a system where surfactants from both an oil and aqueous phase are adsorbing to an interface, electric fields can be used to rapidly transport the oil-soluble surfactant to the interface. By controlling the time and duration of application of the field, one could engineer interfaces having different chemical compositions, resulting in interfaces with distinct interfacial mechanics. Further, instead of using a constant electric field, the effect of a time-varying field could be probed, as this is more relevant to electrocoalescence<sup>3,4</sup>.

Chapter 6 also shows that interfacial tension measurements are a more sensitive tool to determine the presence of charged species in a nonpolar medium. A theoretical or computational model to analyze the transport of surfactants under electric fields might be useful to estimate the charge or concentration of the charge carriers. One approach could be to assume a certain charging mechanism, and solve for the mass transport of the surface active species using a diffusion model, along with electrophoretic transport of the species under electric field. This needs to be solved in conjunction with the equation of state and adsorption isotherm to predict the dynamic interfacial tension. Data from experiments can first used to obtain the equation of state and adsorption isotherm, and then be directly compared to the prediction from the model. The charge and concentration of the species can be obtained as fit parameters.

Finally, a new direction for the field is to account for the solubility of surfactant or interfacial rheology, or both, in developing computations for drop deformation. This would first require measuring the interfacial mechanics under electric fields to ascertain if electric fields change interface moduli. Effects of interfacial rheology will manifest in the interfacial stress balance conditions. Understanding how the mechanics of the interface affects drop deformation and breakup will be useful in informing the design of both materials and operating conditions of electrocoalescers and electro-emulsifiers.

# Appendix A

## Convergence tests for chapter 2

Here, we present a convergence analysis to select the number of elements, N, into which the top half of the drop is partitioned, and the time step size,  $\Delta t$ . For this analysis, we select the first  $PR_A$  drop with (M, S, R) = (1, 1, 0.05)at  $Ca_E = 0.28$  and  $Re_E = 0.15$ . We test three values each for N and  $\Delta t$ . The results of the computations for the different cases are shown in Figure A.1. Changing the values of N or  $\Delta t$  does not significantly alter the result. Moreover, all the values tested predict the formation of conical tips to be the mode of breakup, confirming that this is not a numerical artifact. We fixed N = 150 and  $\Delta t = 0.05$  in all the computations presented in the main sections of the paper.



Figure A.1: Convergence results for a  $PR_A$  drop with (M, S, R) = (1, 1, 0.05) at  $Ca_E = 0.28$  and  $Re_E = 0.15$ . Deformation of the drop as a function of the dimensionless time for (a) different values of N at  $\Delta t = 0.05$ , and (b) different values of  $\Delta t$  at N = 150. Drop shapes before breakup for (c) different values of N at  $\Delta t = 0.05$ , and (d) different values of  $\Delta t$  at N = 150.

# Appendix B

## Convergence tests for chapter 3

Here we present a convergence analysis to select the number of nodes, N, into which the top half of the drop is partitioned, and the time step size,  $\Delta t$ . For the system considered here,  $(M, S, R) = (1, 8.16, 5.1 \times 10^{-10})$ , and the convergence tests were performed for a uniform D.C. electric field at  $Ca_E = 0.24$ . The results are shown in Figure B.1. Increasing N beyond 150, and reducing  $\Delta t$  below 0.02 does not significantly change the predicted final deformation before breakup. Moreover, all the chosen N and  $\Delta t$  predict breakup with the formation of pointed ends, confirming that this is not a numerical artefact. In all our computations, we fixed N = 150 and  $\Delta t = 0.02$ .



Figure B.1: Convergence results for the system under a constant electric field at  $Ca_E = 0.24$ . Final deformation before breakup for (a) different values of N at  $\Delta t = 0.02$  and (b) different values of  $\Delta t$  at N = 150.

# Appendix C

# Coefficients of the $\mathcal{O}(Pe)$ solution

Below are the expressions for the coefficients A, B and  $D_i$  of the  $\mathcal{O}(Pe)$  solution to the bulk surfactant concentration, interface surfactant concentration, and the flow field inside and outside the drop (equations (4.25) - (4.30)):

$$A = \frac{3h\Gamma_0}{2(\lambda+1)} \left[ 1 + \frac{3\{2+hDa(1-\Gamma_0)\}}{DaD_r(C_0+k^{-1})} \right]^{-1}$$
(C.1)

$$B = \frac{\Gamma_0 D_r}{2(\lambda+1)} \left[ 1 - \left\{ 1 + \frac{3\{2 + hDa(1-\Gamma_0)\}}{DaD_r(C_0+k^{-1})} \right\}^{-1} \right]$$
(C.2)

$$D_{1} = -\frac{21\Gamma_{0}D_{r}Ma(1+\Gamma_{0}+\Gamma_{0}^{2})}{10(\lambda+1)^{2}} \Big[1- \Big\{1+\frac{3\{2+hDa(1-\Gamma_{0})\}}{DaD_{r}(C_{0}+k^{-1})}\Big\}^{-1}\Big]$$
(C.3)

$$D_2 = -\frac{D_1}{7} \tag{C.4}$$

$$D_3 = \frac{2}{7}D_1 \tag{C.5}$$

$$D_4 = -\frac{5}{21}D_1 \tag{C.6}$$

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