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The Effect of ethylene glycol dimethacrylate and sodium lauryl sulfate surfactants on droplet characteristics in inkjet printheads

Dawn Api

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THE EFFECT OF ETHYLENE GLYCOL DIMETHACRYLATE AND SODIUM LAURYL SULFATE SURFACTANTS ON DROPLET CHARACTERISTICS IN INKJET PRINTHEADS

by

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A Thesis Submitted in Partial Fulfillment of the Requirements for the
MASTER OF SCIENCE IN MECHANICAL ENGINEERING

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August, 1999
FOREWORD

Always first in my life, I would like to thank my family. Without their undying support, passive guidance, and faith in me, I could never have accomplished all that I have academically or otherwise. My parents are my number one inspiration and role models, and my brother is my best friend. They are among the only ones who never lost their patience with me on my long pursuit to finish this work. Thank you for enabling me always to follow my dreams, even 300 miles away from home.

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Thinking back, I feel the need to thank several people who were quite influential in the beginnings of my technical pursuit. Ms. Trudy Keane, Mrs. Pallero, and Mr. Hainbridge from Cardinal Spellman High School who recognized and developed the skills I have since incorporated into engineering.

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- Dr. C. Haines, for giving me the opportunity to pursue the BS/MS program
ABSTRACT

The purpose of the present experimental work is to determine the surface tension of various surfactant solutions using the capillary method and observe droplet ejection behavior for these solutions in order to define the correlation between the two.

The present work examines the role of surfactants in inkjet printing. One of the most important properties of inkjet ink is surface tension, and surfactants are used in ink to control this property. Specifically studied in this investigation are different concentrations of the surfactants ethylene glycol dimethacrylate and sodium lauryl sulfate. Surfactants have been ejected using a piezo inkjet printhead, and the behavior of the resulting droplets has been studied with respect to their geometry, repeatability, and potential effect on print quality. All behavior is related to surface tension, so this property has been experimentally determined for all concentrations of surfactant using the capillary method. A commercial grade ink was used as a baseline against which to judge different surfactant concentration droplet behavior.

Surfactants having too low of a surface tension showed problems with ingestion (air bubbles in the exit nozzles) and droplet geometry, while those surfactants with excessively high surface tension had difficulty firing at all. The 8.6% ethylene glycol surfactant displayed characteristics most similar to the baseline commercial ink sample.
NOMENCLATURE

B = bias limit

g = gravity (9.81 m/s²)

Δh = change in height due to capillarity

m = mass of surfactant

P = precision limit

r = inner radius of capillary tube

U = uncertainty limit

v = volume of surfactant

Greek Letters

θ = contact angle

ρ = density of surfactant

σ = surface tension
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1. Introduction

Printing technology has undergone dramatic changes to keep up with the developments in personal computers. Different types of printing technologies have been developed, the three major being: dot matrix, inkjet, and laser. The earliest form of printing, dot matrix involves hitting an ink-soaked ribbon with a vertical column of pins. Inkjet printing has enabled improvements in desktop printing, allowing faster speeds, quieter operation, and higher print quality by firing ink out of an array of small nozzles. Lastly, laser printing provides the highest print quality and fastest print speeds, but at a high cost to the consumer, since laser units essentially operate in the same way as a photocopier.

1.1 Printer Overview

There are many types of printers on the market today. Besides varying in size, print speed, and print resolution, the very technology that drives the printers can vary greatly. The low-end color printing market is currently dominated by inkjet based products. Far superior to the noisy dot matrix printers of years past, which produced inferior image quality and had no capability for color, the inkjet printer is quiet, fast, and has achieved high levels of resolution. Improvements of both hardware and software have enabled resolution of up to 1440x720 dots per inch (dpi) and up to nine pages per minute print speed. In 1990, these numbers were 360x360 dpi and up to two pages per minute (Bains, et. al., 1990). Microelectronic and mechanical system technologies have enabled inkjet applications to
achieve a low cost to performance ratio. This is in contrast to laser printing, which has not been able to compete with inkjet on the low-end market because of the cost, particularly where color is concerned.

1.2 Inkjet Principles and Methods

Specifics of inkjet operation are discussed in this section, as well as the very important role of ink in inkjet printing. Surface tension plays a major role in the behavior of the ink, so specific attention is focused on the effect of surfactants.

Though there are different types of inkjet printers, the basic operation is the same. The ink resides inside the reservoir of a printhead until it is physically ejected by a forcing mechanism out of a nozzle and onto media, such as paper or a transparency. The distinguishing factor between different types of printers is the forcing mechanism, as inkjet printers can be driven either thermally or by use of a piezo crystal. In either case, there is a strong dependence of ink on the technology and architecture of the ink path and ejection site. Thermal inkjet printers eject their ink through nozzles by the rapid heating of liquid in a channel, which creates a vapor bubble that displaces the ink out of the nozzle. The ink in a piezo printhead is displaced through the motion of a diaphragm. In both cases, the input signal that triggers the displacement is an electrical signal, and momentum from that displacement is transferred to the surrounding ink, causing ejection. In piezo inkjet, electrical signals are provided to the piezo crystal, which responds with a rapid deformation that
physically pushes the ink out of the printhead. The electrical signals that each printer uses for firing timing are programmed into the software that controls the printer. A diagram of piezo actuation follows:

**Piezo Printhead**

A piezoelectric printhead uses a special type of crystal that responds to electrical current.

When a charge is applied, such a crystal deforms slightly. In a printhead, the crystal's movement forces a tiny droplet of ink through a capillary tube.

When the current is removed, the crystal snaps back to its original position.

*Figure 1.1 - Piezo Inkjet Operation (Source: Epson.com)*

A thermal inkjet printhead operates similarly except that in the place of the diaphragm as seen in the picture shown above, a vapor bubble is formed as a result of the lower part of the channel being heated rapidly to high temperatures. The air displacement of the bubble causes the same ink reaction as the diaphragm.

In most inkjet applications, the front face of the printhead is coated with a hydrophobic (water-resistant) film, which decreases the tendency of the liquid ink to adhere to the surface, which, left uncontrolled, would cause severe misdirectionality and misfiring problems.
1.2.1 Role of Ink

Ink plays a significant role in inkjet printing in that it must be optimized for a given printer architecture. The ink and the printer are, as a design practice, developed simultaneously to obtain the best relationship between the two. Control over printhead location as it prints across a page becomes much less valuable in the design if the ink drop volume and behavior are not controlled. Viscosity, surface tension, solubility, and many other factors are very important in choosing an ink for a printer. The role of surface tension is discussed next.

1.2.2 Surface Tension in Inkjet

Surface tension plays an important role in inkjet because the behavior of the droplets both at the nozzle exit and en route to the media depends greatly on surface tension. There are other factors that contribute to the behavior of ink droplets, and though other ingredients are put into the ink besides surface active agents, surface tension is a particularly significant factor in ink chemistry since it potentially affects print quality during all stages of droplet development. More specific ways that surface tension can affect print quality are discussed next.

1.3 Image Quality in Inkjet Printing

Image or print quality in inkjet printing are what have led to the success of the technology. By controlling factors in the ink as well as in the software of inkjet printers, maximum resolution and optical densities
may be achieved. In theory, the smallest nozzles and the darkest inks would respectively produce the best resolution and the highest optical density. However, the constraints against these optimizations are great, and in attempting to obtain the highest print quality, there are many other factors that must be controlled. In observing droplets, the potential for producing 'good' or 'bad' prints can be predicted by looking at the following factors in a droplet’s trajectory: droplet size and shape, droplet imperfections (such as satellites or tails), how quickly the droplet recoils out of the nozzle into a spherical droplet, and interference effects. These physical characteristics are discussed in more detail next.

1.3.1 Droplet Size and Shape

Droplet size is very dependent on surface tension because as the droplet is leaving the nozzle exit, a necking or pinching must occur so that the droplet can break off. Necking is shown in Figure 1.2 below.

![Figure 1.2 - Droplet Showing Necking](image)

Oversized droplets are a result of this necking occurring too late, which typically is the case for surfactants with very low surface tension. Surface tension is the force that causes the droplet to break off into a spherical shape, and when the droplet is oversized, it takes longer for surface tension forces to pull the droplet into a tight sphere. Recall that
the surface tension is a result of surface free energy per unit area. Thus, larger area in an oversized droplet makes higher surface free energy necessary for the surface forces to act in the droplet. The result of an oversized droplet is a decrease in the resolution in a print. The printing industry has been achieving smaller and smaller drop sizes, which has enabled better and better print quality. It is for this reason that large droplets are troublesome. A final reason that oversized drops are unfavorable for print quality is that the excess ink on the media due to an oversized drop creates opportunity for image smudge or smear.

Along with the problem of oversized droplets is that of non-spherical droplets. Often the two are tied together, in that an oversized droplet tends to have more difficulty, as discussed just earlier, pulling into a tight sphere before contacting the media. A further issue with odd-shaped droplets is their eccentricity. All droplets have an intended trajectory or path upon exiting the nozzle. Factors such as printer carriage motion, distance to the media, and ejection timing are all configured such that ejected droplets hit their intended target within a certain tolerance. The center of mass in an oblong shaped droplet tends to allow its trajectory to be affected, resulting in an oversized droplet (see above for detriment to print quality from that alone) that is also off-course. Therefore, it is important for print quality that the size and geometry of ejected droplets be controlled.
1.3.2 Satellites/Tails

Satellites are small drops of liquid that trail behind or along side of the main ejected droplet. A small satellite is shown in Figure 1.3.

![Figure 1.3 - Ejected Droplet with Satellite](image)

Satellites can be caused by two aspects related to surface tension: if the surface tension of the liquid coming out of the nozzle is very low, it is likely that the satellite is caused by liquid either breaking off the main droplet (not enough force to hold it together) or liquid that remained in the nozzle falling out after the droplet breaks off due to there not being enough surface tension force to hold it in to the nozzle. On the other hand, for a higher surface tension liquid, the satellite could be liquid that gets drawn in toward the main droplet as it is ejected and stays separated from the large droplet. This explanation of the possible causes of satellites due to surface tension can be equally applied to tails. The tails, like the satellites are due to excess liquid trailing behind the main droplet. The difference with tails is that the excess liquid is physically attached to the main droplet. This, again, can be due to ‘fallout’ with low surface tension surfactants, or ‘pulling’ of higher surface tension surfactants.
There are several possible results of satellites and tails. If a droplet is ejected with a tail or satellite, one of two things may be occurring: either the droplet is undersized, and the tail or satellite completes its volume requirement, or the droplet is of the correct size, and the tail or satellite is in excess of the volume requirement for that droplet. In the case where the satellite or tail completes the volume of an ejected droplet, the results are likely more favorable. In this case, at least the volume of ejected surfactant is correct. However, there is the chance that the satellite will follow a different trajectory or that the tail will separate from the body (becoming a satellite) and will take a different path. In this case, the satellite causes an artifact on the media. An artifact is defined as any ink or particle which occurs where it should not. The case of a droplet of a correct volume with a satellite or tail has a problem in addition to artifacts. If the satellite or tail becomes incorporated into the main body, the droplet become oversized and encounters problems like those described earlier with oversized droplets. Figure 1.4 shows a droplet with a tail behind it.

![Figure 1.4 - Two Droplets with Different Tails](image)

In addition to the chance of artifacts, there is also a chance of incorrect droplet size when satellites and tails are present. Satellites and
tails may occur as a result of optimizing other aspects and properties of the ink. The difficulty is controlling both the droplet and its excess.

1.3.3 Recoil

As just discussed, one outcome of an ejected droplet carrying a tail behind it is the tail’s separation from the main droplet. A second, and more favorable, outcome is the recoil of the droplet. Recoil is the drawing of the tail into the main body of the droplet. Recoil results in a more favorable drop shape, though not necessarily a more favorable drop volume. Surface tension forces are responsible for this action, and at times the inward pull 'snaps' the droplet into shape very quickly, resulting in a rebound effect. A rebound effect is a reverberation of the droplet due to surface tension. The drop changes shape without changing its volume. This is fine from a drop volume standpoint, but unfavorable from a print quality standpoint if this reverberation occurs for an extended period of the droplet's path to the media. The uneven and changing geometry of the droplet affects its trajectory and possibly its shape on contact of the media. This 'snap' is more likely to occur in an ink having a higher surface tension.

1.3.4 Surface Droplets and Other Interference

Also more likely to occur with inks containing higher surface tension surfactants are surface droplets. Surface droplets are excess liquid on the surface of the nozzle face which interfere with the normal ejection of
the droplets. Further, there is a possibility of this excess liquid on the surface falling to the media, creating a spot much larger than the ejected droplets. Pictures of surface interference are shown below.

![Figure 1.5 - Surface Liquid (1) and Surface Droplet (2)](image)

A troublesome byproduct of low surface tension inks, on the other hand, are air bubbles. Low surface tension at the boundary layer allows the mixing of air and liquid, and when the air remains in the solution as air bubbles, there is a detrimental effect on droplet ejection. Air bubbles clog the small nozzle exits on the printhead and the result is fewer ejection nozzles firing when they should. The effect on print quality is that misfires lead to deletions, which are white spaces where ink should be.

There are other types of interference, mostly not having to do further with the surfactants themselves, but more to do with particles that become obstructions in the nozzle. Surface tension still plays a role in that with a lower surface tension surfactant, the liquid may be able to move through the nozzle by breaking up and going around the particle. This is not as likely for a surfactant with higher surface tension, since the liquid would tend to stay coalesced and thus become blocked in the
1.3.5 Other Factors of Image Quality Relating to Surface Tension

Inkjet inks are optimized for not just their firing and trajectory behavior, but also for the intended media. Surface tension affects the rate at which an ink gets absorbed into the media. Lower surface tension causes ink to absorb quickly, which is a positive attribute from a speed standpoint. Quick absorbing inks dry on most types of papers more quickly. However, low surface tension, quick absorbing inks are detrimental to print quality. Print quality decreases as ink absorbs into the fibers of paper, causing the fibers to swell. The ink tends to follow the lengths of the fibers, thus spreading the image, which decreases sharpness and optical density, and increases the potential for intercolor bleed. Thus there is typically a compromise between the quick drying, low image quality, low surface tension inks and their counterparts which are high surface tension and therefore higher image quality, though more slowly drying. All of these effects are considered in ink in addition to the ink’s behavior as it is ejected from a printhead.

1.4 Role of Surface Tension in Inkjet Applications

This section provides an introduction to surface tension, the capillary effect, and surfactants.

1.4.1 Surface Tension

Surface tension is the force by which a droplet of liquid holds itself
Together. The equilibrium shape of a volume of liquid is one that has a minimum area. Forces acting in the plane of the surface of the droplet tend to minimize the area, resulting, in most cases, in a spherical droplet. Surface tension depends mainly upon the forces of attraction between the particles within the given liquid and also upon the gas, solid, or liquid in contact with it. All molecules in a bound region (such as a droplet) are subject to an attraction force normal to the surface or interface. In the case of a droplet ejected from an inkjet nozzle, the interface is formed with the air around the droplet. Molecules on the surface of the liquid are in a one-sided force field pulling them back into the bulk of the liquid. As molecules are extracted from the surface layer, those remaining at the surface have increased intermolecular distance between one another, drawing the overall surface into a smaller area. The stronger the attractive force toward the bulk, the higher the surface tension is. Thus, surface tension is the stretching force at the surface of the liquid.

Work is required to bring molecules to the surface of a liquid. Surface free energy is the work required to create 1cm² of new liquid surface. Put in other words, surface free energy is the work required to transport enough molecules from the bulk to cover 1cm² of surface. Surface tension can be expressed as free energy per unit surface area. Thus, as the surface area of a droplet gets smaller, the amount of work needed to move the molecules to or from the bulk decreases for a constant value of surface tension. Likewise, looking at liquids with
different surface tensions, liquids with a higher surface free energy would tend to have a higher surface tension. Units for surface tension observed in this way are erg/cm² or mJ/m². As a function of force per unit length, units are dyne/cm or mN/m.

When the droplet reaches its smallest size, it is said to be at equilibrium. This equilibrium, however, is a dynamic equilibrium. Molecules continue to exchange at the liquid / vapor interface, within the boundary region (since it has a thickness), and between the surface region and the adjacent layers of liquid in the droplet. Temperature affects the behavior of the molecules, however, and is therefore inversely proportional to surface tension. For example, the surface tension of water varies from about 0.074 N/m at 20°C to 0.059 N/m at 100°C.

1.4.2 Capillary Effect

Capillary attraction is caused by surface tension. The adhesion between liquid and solid is relative to the cohesion of the liquid to itself. Therefore, surface tension can be measured by observing capillary attraction. Wettability refers to a liquid’s ability to adhere to a solid. When a capillary tube (a tube of small known diameter) is placed into a volume of liquid, the liquid ‘climbs’ up the glass, rising above the level of the main liquid volume, forming a meniscus at the highest point. Higher surface tension liquids have a higher wettability and thus climb higher in the tube. Menisci at these high points are either concave up or concave down, depending on the contact angle at the liquid-solid-gas interface. Most
liquids have a concave up meniscus, while mercury is an example of a liquid that does not. The picture below shows this difference in capillarity.

![Image](image.jpg)

Figure 1.6 - Capillary Menisci and Other Factors for Calculations (Source: Encyclopedia Britannica Online)

The image above show some of the factors needed to calculate surface tension such as the height, $h$, and the contact angle (not labeled), which is the angle that the liquid makes with the glass at the air interface. The angle of the air-liquid-water interface is highly dependent on wettability and thus, surface tension.

1.4.3 Surfactants

Surfactants are also referred to as surface-active agents. When added to a liquid, surfactants reduce the surface tension of that liquid. In doing so, the surfactants also increase the wetting and spreading
properties of the liquid, which is why detergents and cleaning supplies contain surfactants. Surfactants are used in inkjet applications in the ink formulation for a variety of reasons.

1.5 Objectives of the Present Work

The purpose of the present experimental work is to determine the surface tension of various surfactant solutions using the capillary method and observing droplet ejection behavior for these solutions in order to define the correlation between the two.
2. Literature Review

Inkjet printing technology entered the low-end desk printing market in the late 1980's, and since then, the focus has been toward improving the print quality and speed. In the present work, the specific research directed at print quality as related to droplet characteristics in inkjet printing is reviewed.

2.1 Drop Generation Process in TIJ Printheads

Ohoro, et. al. (1996) conducted a survey with the purpose of qualifying that the behavior of drop generation was in good agreement with their 3D fluid flow calculations. This drop generation is accomplished using a thermal inkjet printhead, which has similar characteristics to the piezo inkjet printhead used in the present work. The behavior was studied specifically with respect to the problem of ingestion, whereby air penetrates into the channel to cover a portion of or the entire heater of a thermal inkjet printhead.

Ohoro, et. al. provide an excellent background, explaining the basic principles of thermal inkjet printhead operation. An electrical firing pulse is given to the heater surface, which superheats and forms a vapor bubble in the same way that the pulse with a piezo causes a deflection in a diaphragm to displace ink out of the nozzle. A diagram is given below showing the cross-section of a thermal inkjet nozzle.
Figure 2.1 shows the entire micromachined assembly of a thermal inkjet printhead nozzle. Ink enters the printhead nozzle from the right side in the picture, and flow is from right to left. The bypass plug shown in the figure is a means of modulating the flow into the nozzle, and the different pits are ways of modulating the flow once in the nozzle. Ink must be held stationary in the nozzle until the vapor bubble is formed in the heater pit. This vapor bubble pushes the ink through the channel and out of the printhead.

After the ink displacement due to the piezo or vapor bubble, the meniscus retracts into the nozzle and ink refills the chamber. It is during this retraction that ingestion tends to be a problem. Specifics of ingestion are discussed next.

In the case of thermal or piezo inkjet, the composition of the ink and therefore, the properties, are very important in discouraging ingestion. At higher firing frequencies (i.e. - faster print speeds) and higher
temperatures, ingestion tends to occur more often. Ohoro et. al.’s literature describing this study does not proceed further in the explanation of this phenomenon. This explanation will follow. The problem ingestion causes, and the reason it is to be minimized, is that the air bubbles that become mixed into the ink act as particles which block the exit nozzles, causing misfires and erratic drop behavior. The ingested bubbles absorb the displacement momentum of the piezo diaphragm (in piezo printheads) or the vapor bubble (in thermal printheads).

The experiments were conducted by Ohoro, et. al. such that all phases of the droplet ejection and the potential ingestion could be observed. Various phases of vapor bubble growth/collapse, drop ejection, meniscus movement, and channel refill were measured and the process was recorded on video. Processes were studied as a function of temperature. The ink used was a dyeless water-based ink containing 20% 1,2-ethanediol (ethylene glycol dimethacrylate) and 3.5% 2-propanol. In order to predict bubble behavior, fluid flow calculations using FLOW3D analysis code along with 1D thermal code were used.

Results and discussion were given with respect to ingestion and channel dropout, which is the condition by which the nozzle ceases to fire due to ingestion. It was concluded that at temperatures up to 65°C and firing frequencies up to 4.5kHz, the meniscus retracted back into the nozzle without outside air entrapment, channel dropout, or degradation of drop properties.
The literature of Ohoro, et. al. does not discuss the cause of the air entrapment, though it is mentioned to be a result of ink properties. Specifically, air entrapment and the consequent ingestion occur when the surface tension of the ink is low. Surface tension decreases with increasing temperature, so it is not surprising that higher temperatures caused more problems with ingestion. As discussed in Chapter 1, at higher temperatures, the surface free energy of the liquid is lower, the meniscus is weaker, and there is more mixing of liquid with air across the boundary layer. Higher frequencies further aggravate this mixing problem, and the result is air entrapment. The present study uses the same ink formulation proportion and later discusses low surface tension/ingestion as an issue with studying droplet behavior.

2.2 The Influence of Surfactant Structure on Ink Detachment

Rao, et. al. (1998) provide an extensive discussion on surfactants with respect to the fact that they facilitate the separation of ink from paper. Polyethylene-oxide ether surfactants are used to release ink from paper fibers, and it is found that the efficiency of this release is strongly dependent on the ink chemistry. Looking for complete release of the ink down to the lowest stratifying layers, Rao, et. al. designed the experiments to separate the release effects resulting from mechanical forces (shear and vibration) and chemical treatments.

The background provided by Rao, et. al. discussed the ink/media interaction and its potential effect on separation ability. Printing inks, the
literature states, are specifically formulated with the intent of controlling their drying properties and ink/substrate interactions. Strong physical interactions and chemistry changes occurring in ink will increase the stress required for complete detachment. Thus the efficiency of ink removal from the substrate is affected by wettability of the ink, as well as factors such as the thickness of the print, and the repulping conditions of the paper. Detachment efficiency is thus characterized as the amount of removal with respect to the amount of energy put into the system.

The study explains that ink detachment occurs in two stages: First is the release or softening of the ink, which is governed by chemistry and intermolecular interactions and this occurs spontaneously. Next, the detachment requires more energy because separation occurs on the particle level. This is where the role of surfactants is introduced, in that removal of the lowest stratifying layers involves the use of surfactant. The complete release of ink from substrate surfaces, however, requires not just surfactants, but mechanical action as well.

For the experiment in their report, Rao, et. al. used a cellophane model substrate, and the model ink was oil-based news ink. Use of surfactant enabled the maximum detachment efficiency in all cases, and they found that the rate of this detachment can be significantly increased by changing the properties of the surfactant. A specific properties of surfactant named to have this effect was hydrophobicity. Specifically, increasing the hydrophobicity would be expected to increase the rate of
detachment. Complete release of the ink requires some mechanical action, however, and although the process can be achieved using just chemicals, the process is quite slow. The authors concluded that the efficiency of ink release from substrate fibers increases with decreasing hydrophilicity and molecular weight. Several of the graphs supporting this data are shown below.
This research is relevant to the present work in that it highlights a favorable effect of surfactant. That the ink detaches more easily by the use of surfactant is a benefit with respect to the media for this research. However, the high concentrations which allow this behavior are unfavorable from a droplet behavior standpoint, since lower surface tensions (from higher concentrations of surfactant) tend to have problems
with ingestion. This literature is an example of the many other factors besides droplet behavior that must be optimized by use of surfactants.

2.3 Dependence of Surface Tension of Surfactant Solutions on Drop Size

Bianco and Marmur (1992) discussed in this publication the effect of large surface area on surfactant surface tension. They found that surface tension of drops begins to deviate from that of the original solution for drops smaller than about 10μm in radius, which is typical of aerosols and emulsions. This is significant to the present work in that it validates the assumption that droplet surface tension can be characterized by its behavior. The present work discusses droplets of larger size than 10μm.

The authors explain that when the surface area of a surfactant solution is greatly increased by creating small droplets, the surface tension with respect to the original solution depends on the droplet size. The amount of surfactant in each particle is finite, thus size of the droplet plays an important role in characterizing the droplets. However, for large enough droplets, behavior can be deemed predictable by the fact that each droplet presumably contains the same percentage of surfactant by weight. Testing and calculations were performed using sodium dodecyl sulfate (SDS). The graph below shows the dependence of the bulk concentration of a drop of SDS solution on its radius.
Small droplets as discussed in this research tend to be described as atomizations or emulsifications, which come from a given volume of surfactant. Thus their surface area is greatly increased by the emulsification process. In a case such as this, interfacial energy is increased with no change to the original surfactant concentration. The report considers the condition of constant mass of surfactant, stating, 'under conditions of constant mass of surfactant, the extension of the film interfaces leads to a reduction in the surfactant concentration inside the film, as well as on its interfaces'. Therefore, because of redistribution of surfactant molecules between the bulk solution and the interfaces of the film, surface tension increases when the film is extended. This is as expected, since each small droplet contains the same amount of surfactant but has much higher surface area compared to the original solution. Thus
the surface tension is increased. Equations supporting this information are based on linear approximation for very low concentrations, and the following chart depicts the dependence of the surface tension of a drop of SDS solution on its radius.

![Chart: Dependence of the surface tension of a drop of a SDS solution on its radius. The numbers indicate the values of \( c_m / a \).](image)

Figure 2.5 - Dependence of surface tension of drop to its radius (Bianco and Marmur, 1991)

This literature shows that an analogous effect exists when the surface area of a surfactant solution is increased to a large extent in finite systems, as it was for the present work.

2.4 Scope of the Present Work

In the available literature, there is not clear characterization of droplet behavior at and immediately following the ejection. Since the droplet behavior at this stage is critical to print quality, the present work
reported in this thesis is aimed at defining the droplet characteristics and identifying their relationship to surface tension of the ink. This is achieved by using deionized water with either ethylene glycol dimethacrylate (1-15% by weight) or sodium lauryl sulfate (0.05-0.5% by weight) as surfactants. It was using these surfactants that the droplet ejection process was recorded and analyzed. Capillary measurements and calculations provided values for surface tension, and it was against these values that the behavior was judged in order to determine the role of surfactants on surface tension in inkjet applications.
3. Experimental Setup

3.1 Overview

The two major aspects of the experimental setup were formulating the surfactants and assembling a working system with which to fire and observe surfactant droplets. The following sections describe the details of the setup as well as the concentrations and types of surfactants studied.

3.2 Equipment

Both hardware and software were utilized to run the printhead and later acquire the images necessary to characterize droplet behavior. Most of the hardware setup is shown below in Figure 3.1.

![Experimental Setup](image)

Figure 3.1 - Experimental Setup

What is not shown in the picture, but is later explained in more detail, is the shelving that was necessary because of the short length of the pin cable from the printhead. However, each of the functional
components is shown and explained in more detail in this section.

3.2.1 Components

3.3.2a Liquid Supply Line

A Pyrex bottle, with a screw-on lid with an air inlet and a fluid outlet provided the means for increasing the pressure and filling the piezo cavity with liquid. Thus, when the bulb was squeezed, pressure was introduced into the container, forcing liquid down the long tubing and into the module. Once the piezo cavity had been filled with surfactant, the crystals were fired and the pumping of liquid occurred automatically. A picture of the liquid supply line is shown below.

![Liquid Supply Line](image_url)

Figure 3.2 - Liquid Supply Pump and Line

3.3.2b Observation / Mounting Apparatus

An ABS plastic Radio Shack box was chosen as the mounting apparatus for the module. This box was chosen for a number of reasons. First, the box could be closed off with a Plexiglas cover, which allowed for direct observation of the droplet
ejection zone, while allowing a contained area in which to collect the used surfactant. A section was easily machined out of the Plexiglas to allow for the microscope lens to fit close to the nozzles for observation. Likewise, the ease of machining was a benefit of the ABS plastic box as well. A slot was milled into the plastic as a locator for the module. A drain was designed at the bottom of the box in order to efficiently remove surfactant after each section of data acquisition. In between surfactants, the box was cleaned thoroughly using tap water, followed by deionized water. After the box was rinsed it was allowed to dry completely before studying the next surfactant. The apparatus used as a test stand for this experiment is shown below.

![Figure 3.3 - Apparatus with Module](image)

### 3.3.2c Piezo module / Components

A generic inkjet head was used to generate the surfactant droplets studied in this experiment. The head consisted of a row of ink nozzles to be fired by piezo crystals. Each nozzle was a small opening out of which the droplets were formed. The head
contained an inlet valve for the intake of ink. Timing and signals were provided by a PC attached to the module by a ribbon cable. Other electronics were on the head, but for the purpose of this experiment, these components will not be discussed in detail. A non-detailed picture of the module is shown below.

![Module in Apparatus with Ink Supply](image)

**Figure 3.4 - Module in Apparatus with Ink Supply**

3.3.2d Lighting

Lighting was a major consideration in the observation of the drops, since higher magnifications of the microscope made it more difficult to transmit light. A white light source was used to position the ejection chamber of the module so that the initial formation of the drops could be observed. This light source was aimed at the module from the outside, rather than through the microscope, since this achieved the highest intensity light. During the actual experiment and filming, a stroboscope was used. At a frequency of 100Hz, the strobe slowed, and ideally froze, the image of the droplets. This allowed for the observation necessary to make conclusions regarding the behavior of the droplet. The 100Hz
frequency was used for all surfactants during all parts of the observation. A curved glass lens was placed on the emissive surface of the strobe to further increase the intensity of the strobe by focusing the beam onto the module.

3.3.2e Microscope

The magnification used on the microscope which provided the highest quality image was 25x. Lower than that magnification, there was not enough detail seen, and higher, not enough light. The microscope had its own base, but it unfortunately had no x and y adjustments. Therefore all adjustments had to be made to the module and the housing. This was achieved by shims and careful motion of the apparatus and module. The microscope is shown below as it was set up during testing. Here can be seen the way in which the microscope was coupled with the apparatus.

![Microscope Image](image-url)

Figure 3.5 - Camera, Microscope, and Apparatus

3.3.2f Droplet Ejection PC
A computer was used to activate and deactivate the piezo crystal firings, which in turn created the droplets studied in this experiment. The computer is the one shown in the image above, on the shelf. Settings to control the number of active nozzles as well as the system frequency were contained on this computer. The computer was connected to the module by a ribbon cable.

3.3.2g Shelving

The basis for the setup as a whole was not due to space considerations (though it did maximize workbench space), but instead due to the fact that the cord which activated the module was only five inches long, and could not be extended. The cord, a small 10-pin ribbon cable, connects the module to the computer, so the computer had to be placed on a shelf directly above the module housing. The highest shelf also provided a place to put the surfactant during the experiments, since the feed bottle had to be higher than the module in order to facilitate the ink firings.

3.3 Image Acquisition

A PC, VCR, video camera, and television were all used to acquire and process images. The computer used to acquire the images is a separate computer than the one used to fire the droplets. For one configuration of testing, the camera and the PC were used to acquire still images using software called ImagePro®. The configuration was set and when the nozzles began generating droplets, ImagePro was used to
freeze the images into snapshots. The difficulty with this method was that it was difficult to adjust the lighting, microscope focus, or nozzle positioning while attempting to 'snap' the pictures at the computer. Though capable of generating quality images, this method proved to be inefficient since only a limited amount of surfactant is available for each firing. This led to a second configuration. Using a VCR to record moving images, and a large screen television to aid in focusing on and viewing the drops, the images created were of much higher quality, since snapshotting the images was done as a second step. The VCR tape recorded the action while any lighting, focusing, and positioning issues were resolved. Afterwards, observing the videotape on the computer, the best sections of footage were snapped into a series of pictures for each surfactant. Later these labeled images would be divided into the category of droplet development that best described the picture. A great tool, the VCR had the ability to freeze frame and slow-advance motion pictures. This allowed for greater accuracy in judging the formation, geometry, and trajectory of the surfactant droplets. The software used to freeze frame these images was again ImagePro.

3.4 Surfactants

Surfactants were formulated so as to cover a broad spectrum of both concentration and surface tension forces. Sodium lauryl sulfate and ethylene glycol dimethacrylate were each mixed with deionized water to form different concentrations of surfactant. The surfactants were
formulated by weight using a Metler balance. Each concentration of surfactant had its own Pyrex® container so that mixing and dilution effects would be minimized. Also used in the experimentation was a commercial grade ink formulation of unknown chemistry. The effects generated while using this ink formulation were quite favorable, and it was these effects which set the standard for achievement of the other surfactants.

Deionized water was studied for the surface tension (capillary) experimentation since it has a known value of surface tension. It could not be fired out of the nozzles, however, since its surface tension was too high. This experimental value for surface tension obtained by performing capillary measurements for deionized water served as a baseline for the other surfactant surface tension measurements. The only other purpose that deionized water served in the experimentation is that it was used to clean the printheads. This water was flushed through the system using pressure induced by the bulb of the ink supply pump. This pressure was greater than that exerted by the piezo crystals, so there was no concern for blockage due to surface tension during this manual cleaning.

3.4.1 Sodium Lauryl Sulfate

This surfactant is also referred to as Dodecyl Sulfate in a Sodium Salt. Sodium Lauryl Sulfate is a substance often found in soap products because of its very low surface tension. The concentrations studied were 0.05%, 0.15% and 0.50% sodium lauryl sulfate by weight.
3.4.2 Ethylene Glycol Dimethacrylate / Propanol

A second surfactant used was ethylene glycol dimethacrylate. This was chosen as a result of literature research. It is often used in inkjet applications as a means of lowering the surface tension of ink. The concentrations of ethylene glycol dimethacrylate used were: 1%, 3%, 5%, 8.6%, and 15%. The 8.6% concentration was based on an exact concentration used in a published ink surfactant study, and the proportion of ethylene glycol dimethacrylate to propanol was followed from this published example for other concentrations. Propanol was used in very small proportions in order to make the ethylene glycol more soluble. The ratio of EGM to propanol was 1 : 0.175, so the corresponding amounts of propanol added to the surfactants above are: 0.175%, 0.525%, 0.875%, 1.50%, and 2.63%. A 20% / 3.5% solution of ethylene glycol dimethacrylate/propanol was also formulated, but this surfactant reacted very poorly in the nozzles and testing apparatus.

3.4.3 Commercial Grade Ink

Commercial grade ink was used as a standard against which to compare the other surfactant solutions. No properties of the ink were known prior to the start of testing. The ink was a colorless ink, which helped in many aspects of the study.
4. Experimental Procedure

The experimental procedure consisted of the surface tension measurements, drop generation, then drop observation. Surface tension measurements were made using the capillary method, and a piezo inkjet printhead generated the droplets. Images were captured either on video or as computer files and later analyzed. This section explains the methods utilized in creating and observing the droplets.

4.1 Surface Tension Measurements

Before firing the ink surfactants through the jet ejection nozzles, experiments were done to determine the surface tension of each concentration of surfactant. Surface tension can be determined a number of ways, however, the capillary method was used for this experiment.

A thin glass tube (inner diameter = 1 mm) was placed into a known height of surfactant. Capillary action, described earlier, caused the liquid to rise in the tube. This measured height is one component necessary to calculate surface tension. A second component equally important is the contact angle, which is the angle the meniscus of the liquid makes with the face of the glass tube. Density of the surfactant, gravity, and the inner radius of the tube are the final components needed for the calculation of surface tension. The equation below relates all of the components.

\[ \sigma = \frac{r \Delta h \rho g}{2 \cos \theta} \]
Equation 4.1 - Surface Tension Calculation

Where:

\( \sigma = \) surface tension

\( r = \) inner radius of capillary tube

\( \rho = \) density of surfactant

\( g = \) gravity (9.81 m/s\(^2\))

\( \theta = \) contact angle

\( \Delta h = \) change in height due to capillarity

This equation is derived from the free body diagram of the forces present in a liquid filled tube below:

\[
\Sigma F_y = 0
\]

\[
\sigma 2 \pi R \cos \theta - \pi R^2 \rho g \Delta h = 0
\]

Equation 4.2 - Surface Tension Free Body Equations

Refraction effects were taken into consideration when taking capillary measurements, since the curvature of the glass tubing distorts the image of the meniscus. Therefore, for greater accuracy, the outer meniscus was considered. The angle between the glass and the liquid on the inner meniscus was equal to that between the glass and liquid on the
outer meniscus. Therefore the outer meniscus was used for the contact angle in order to avoid any error due to refraction. An example of inner and outer menisci are shown below.

![Image of Inner and Outer Menisci](image-url)

Figure 4.1 - Meniscus Measurement

Height was measured as the change in distance between the surface of the liquid and the meniscus. Results of the above measurements were put into an Excel spreadsheet and surface tension calculated. These results and the comparison to known values for some of the surfactants studied in this testing will be discussed in the results section.

4.2 Drop Generation

The first step toward droplet generation is the setup. The module, ejection nozzles, and inlet tube must be clean and dry. Before the module is plugged into the ribbon cable, it is imperative that the computer that
fires the piezo crystals be off. Power while making any electrical adjustments, according to the manufacturer’s directions, will destroy the module’s electrical characteristics. Once the module is joined with its electrical component, it may be placed into the mounting apparatus.

The next several steps deal with surfactant handling. After choosing a surfactant for study, replace the cap of the Pyrex® glass bottle with the inlet/outlet cap of the liquid supply pump. The long hose of the outlet tube on this cap joins the module. Once this step is taken, it is important to keep the surfactant bottle at a height lower than the module, as otherwise, surfactant will flow through the module by the forces of gravity and be wasted. Since at times it takes up to 50mL to locate a good droplet pattern on the nozzle to photograph, it is important not to lose much surfactant through the nozzles during setup. Most of the surfactants are only present in those glass bottles in quantities of 80mL or less.

With both the surfactant feed and the electrical components of the module ready, the next step was to establish a video image of one kind or another. This mostly involved the camera, VCR, and television. The camera was connected co-axially to the VCR, which processed the image to the television. The white light source was used at this time to locate the microscope to the edge of the ejection face of the module. Once an image was acquired through all the hardware, sharpening the image was typically necessary. Using the Z-plane focus knobs on the microscope,
the image was brought into focus. It was especially important that the focusing be the last step of the setup process because any adjustments to other parts of the system following the focusing of the microscope will cause a loss of image clarity and/or throw off the focus. At this point the module driving computer was powered on. A DOS-based menu on this computer displayed many variables, all of which remained constant throughout this experimentation. The ‘Go' command was given through this menu. However, just before this command was given, the module was manually filled with the surfactant using the liquid supply hand pump. The glass bottle at this point was placed at a height above that of the module, again, allowing for the assistance of gravity in the ejection of the droplets.

4.3 Drop Observation

Once the system was entirely powered up and the module was receiving the CPU signal, a stream of droplets, visible to the naked eye only with the help of a stroboscope, was begun just underneath the nozzle exits. Typically at this point, strobe adjustments would be needed so as to obtain the highest light intensity and thus the clearest snapshots. The strobe frequency used matched that of the droplet ejection at 100Hz. Observing the droplets at this frequency through the microscope allowed the droplets behavior to be better understood, since their motion was greatly slowed by the stroboscope.
At times, the camera would need to be refocused due to shifts that occurred upon initial firing. Also, and more common, often the apparatus would have to be shifted because an active nozzle would fail to fire. The program was set to fire only every 3rd nozzle in order to alleviate interference effects. However, different circumstances would cause the nozzles to misfire or not fire at all, and since the microscope typically only fit three or four nozzles in its viewing area, manual adjustments were often necessary at this stage. Once a consistent stream was being imaged, further focusing provided the sharpest image. When a satisfactory image was obtained, the VCR was turned on to record the droplets. Slowing or speeding the frequency of the strobe gave a good indication of the droplet dynamics once they broke from the exit area. Looking at several streams on the nozzle often developed better understanding of the surfactant behavior across the nozzle. After these droplet behaviors were been recorded to videocassette, the VCR was connected to the ImagePro computer for conversion from motion picture to snapshots and freeze frames. Snapping each frame in a series of drop development provided a valuable tool for later droplet study.
5. Experimental Results and Discussion

The experimental studies were conducted with deionized water and seven surfactant mixtures, 1, 5, 8.6, and 15% ethylene glycol dimethacrylate, and 0.05, 0.15, and 0.50% sodium lauryl sulfate. A commercial grade ink was also studied as a baseline.

The surface tension and contact angle measurements were performed and those results will be first presented (Section 5.2). The majority of this study focuses on the droplet behavior, however, and those results are presented in Section 5.3. Specifically, the aspects of droplet formation, droplet shape at departure from the nozzle, droplet imperfections, droplet recoil, and the effect of nozzle surface liquid are studied.

5.1 Surface Tension Values

The chart that follows gives the calculated values for surface tension obtained using the capillary method. Results have some noise factors and error associated with them, and these will further be discussed in section 6 of this report.
Table 5.1 - Surface tension measurements

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Mass (kg)</th>
<th>Volume (mL)</th>
<th>Density (kg/mL)</th>
<th>ΔH (mm)</th>
<th>Tube Rinner (mm)</th>
<th>θ (degrees)</th>
<th>σ (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI Water</td>
<td>0.05401</td>
<td>54.0</td>
<td>0.00100</td>
<td>26.0</td>
<td>0.5</td>
<td>40.7</td>
<td>0.08408</td>
</tr>
<tr>
<td>SLS 0.05%</td>
<td>0.03275</td>
<td>33.5</td>
<td>0.00098</td>
<td>14.0</td>
<td>0.5</td>
<td>38.0</td>
<td>0.04260</td>
</tr>
<tr>
<td>SLS 0.15%</td>
<td>0.03301</td>
<td>34.0</td>
<td>0.00097</td>
<td>12.5</td>
<td>0.5</td>
<td>31.3</td>
<td>0.03485</td>
</tr>
<tr>
<td>SLS 0.50%</td>
<td>0.03269</td>
<td>33.5</td>
<td>0.00098</td>
<td>9.0</td>
<td>0.5</td>
<td>21.3</td>
<td>0.02312</td>
</tr>
<tr>
<td>EG 1%</td>
<td>0.01005</td>
<td>11.8</td>
<td>0.00086</td>
<td>12.5</td>
<td>0.5</td>
<td>42.7</td>
<td>0.03566</td>
</tr>
<tr>
<td>EG 5%</td>
<td>0.01033</td>
<td>11.5</td>
<td>0.00090</td>
<td>11.0</td>
<td>0.5</td>
<td>28.3</td>
<td>0.02752</td>
</tr>
<tr>
<td>EG 8.6%</td>
<td>0.00996</td>
<td>11.1</td>
<td>0.00090</td>
<td>11.0</td>
<td>0.5</td>
<td>28.7</td>
<td>0.02760</td>
</tr>
<tr>
<td>EG 15%</td>
<td>0.01015</td>
<td>11.3</td>
<td>0.00090</td>
<td>9.0</td>
<td>0.5</td>
<td>21.3</td>
<td>0.02138</td>
</tr>
<tr>
<td>Ink Sample</td>
<td>0.00853</td>
<td>9.3</td>
<td>0.00092</td>
<td>10.0</td>
<td>0.5</td>
<td>34.0</td>
<td>0.02726</td>
</tr>
</tbody>
</table>

5.2 Drop Pictures and Evaluation

Six specific attributes will be studied in the context of droplet behavior for all aspects of droplet development:

- **Droplet geometry** - This refers to the shape, volume, and appearance of the droplet. A small, tight sphere is typically desirable, with no satellites or droplets.

- **Consistency** - This aspect deals with how common or uncommon the behavior related to a specific stage of development is. Consistency relates to drop predictability, which in turn relates to control over where the droplets travel and what behavior they have physically in flight.

- **Interference Effects** - Interference effects refer to anything which interferes with the otherwise uninterrupted generation or trajectory
of a droplet. Examples are anything from a foreign particle or an air bubble in the nozzle to surface liquid on the edge of the nozzle face. Interference effects are unfavorable but at the same time, inevitable.

- Effects of Surface Tension - Without relating specifically to the numerical values of surface tension obtained for the surfactants described in this section, the behavior of the surfactant droplets is explained with respect to the role that surface tension plays in that behavior. In other words, certain behavior indicates that the surfactant might have a low surface tension, while different behavior indicates the opposite. This aspect is described, and in Section 5.4, the correlation between the behavior described in Section 5.3 and the surface tension measurement results given in Section 5.2 will be made.

- Potential Effect on Print Quality - Print quality depends on a great deal more than just the ink itself. Therefore this aspect simply describes the potential way in which print quality may be affected by the behavior observed.

- Non-Surfactant Related Problems Seen - This aspect covers the miscellaneous factors that may have played a role in the behavior of the surfactant droplet. Examples are air currents in the lab, lighting and focus issues, and image acquisition problems.
Following are the droplet pictures and discussion for all stages of development. All are discussed with respect to the six aspects just described. A chart at the end of the section summarizes the behavior of all of the surfactants.

5.3 Results Summary

The following table gives an 'at a glance' review of the above discussion. Ratings are from 1 (worst) to 5 (best) for the categories of geometry, consistence, and potential print quality. The values of surface tension have been added to the table as an introduction into the next section, which correlates the discussion to the experimental values of surface tension. The discussion on the effect of surface liquid has not been included in the matrix below, since it did not apply to all surfactants and had different criteria associated with it. Table 5.1 follows:
Table 5.2 - Summarized Results of Droplet Behavior Observation

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Droplet Formation</th>
<th>Shape at Departure</th>
<th>Droplet Imperfections</th>
<th>Droplet Recoil</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EG 1%</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Geometry (Scale 1-5)</td>
<td>4</td>
<td>3</td>
<td>2 - inconsistent drop size</td>
<td>4</td>
</tr>
<tr>
<td>Consistency (1-5)</td>
<td>good behavior 4</td>
<td>good behavior 3</td>
<td>good behavior 2</td>
<td>good behavior 4</td>
</tr>
<tr>
<td>bad behavior 1</td>
<td>bad behavior 2</td>
<td>bad behavior 3</td>
<td>bad behavior 1</td>
<td></td>
</tr>
<tr>
<td>Interference Effects?</td>
<td>array fire</td>
<td>array fire</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Measured Surface Tension (N/m)</td>
<td>0.03566</td>
<td>0.03566</td>
<td>0.03566</td>
<td>0.03566</td>
</tr>
<tr>
<td>Print Quality (1-5)</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Non-surfactant related problems?</td>
<td>particle in nozzle</td>
<td>particle in nozzle</td>
<td>None</td>
<td>Poor image</td>
</tr>
<tr>
<td><strong>EG 5%</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Geometry (Scale 1-5)</td>
<td>3</td>
<td>2</td>
<td>2 - inconsistent drop size</td>
<td>4</td>
</tr>
<tr>
<td>Consistency (1-5)</td>
<td>good behavior 3</td>
<td>good behavior 2</td>
<td>good behavior 2</td>
<td>good behavior 4</td>
</tr>
<tr>
<td>bad behavior 2</td>
<td>bad behavior 3</td>
<td>bad behavior 3</td>
<td>bad behavior 1</td>
<td></td>
</tr>
<tr>
<td>Interference Effects?</td>
<td>surface liquid</td>
<td>surface liquid</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Measured Surface Tension (N/m)</td>
<td>0.02752</td>
<td>0.02752</td>
<td>0.02752</td>
<td>0.02752</td>
</tr>
<tr>
<td>Print Quality (1-5)</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Non-surfactant related problems?</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td><strong>EG 8.6%</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Geometry (Scale 1-5)</td>
<td>5</td>
<td>5</td>
<td>3 - satellites &amp; tails</td>
<td>5</td>
</tr>
<tr>
<td>Consistency (1-5)</td>
<td>good behavior 5</td>
<td>good behavior 5</td>
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6. Error and Uncertainty Analysis

This section describes errors encountered during the experimentation. Much effort was put forth to minimize contamination and uncertainty error. Where errors were present, their sources and their implications to the data were sought to be understood. The errors in the experiment include those encountered while mixing the surfactants, maintaining the purity of the surfactants, cleaning of the equipment and work area, and errors in calculating surface tension. Following the list below of the potential sources of error in the experiment is a description of the bias, precision, and uncertainty limit.

Sources of error in the experiment were as follows:

1. Mixing the surfactants - Metler balance was used to measure out surfactants for the respective concentrations. The balance gives four decimal places, giving it three digit accuracy. The actual measured proportions of the ethylene glycol dimethacrylate / propanol mixtures were:

   - 1.006% / 0.174% (EG / Propanol 1% / 0.175%)
   - 4.994% / 0.874% (5% / 0.875%)
   - 8.601% / 1.512% (8.6% / 1.5%)
   - 15.045% / 2.622% (15% / 2.625%)
   - 20.082% / 3.495% (20% / 3.5%)

Therefore, at least two digit accuracy was maintained
throughout the mixing process, which in itself was delicate since the amounts were so small.

2. Purity of the Surfactants

The surfactants were kept separate and uncontaminated from one another by labeled Pyrex glass containers. Each surfactant was used only once, in order to avoid contamination resulting from contact with impurities in the printhead. Therefore the images shown in the results and discussion section reflect the true properties of the mixed surfactant.

3. Cleaning of Printhead

Cleaning of the printhead could only be done with deionized water, since simple tap water contains impurities that may potentially clog the nozzles. The deionized water was pumped through the printhead in the same way that surfactant was pumped through. This method cleaned the pumping system, the surfactant delivery lines, as well as the printhead. Afterwards, in order to accelerate the drying of the inside of the small tubes and nozzles in the printhead, an alcohol like propanol or ethanol was pumped through the system in the same way. It was found, however, that this last procedure damaged the printhead, so henceforth, the printhead was dried using air drying, typically overnight.

4. Cleaning of the Apparatus

The apparatus was cleaned using the methods employed in chemistry.
That is, the apparatus was rinsed with tap water three times, followed by three rinses with deionized water. Lastly, a small amount of a drying agent such as methanol was used to accelerate the drying of the apparatus.

5. Capillary Measurements (including cleaning)

Capillary tubes were difficult to clean due to the small inner diameter as well as the tendency of the liquids to stay inside of the tube for various reasons. Therefore for each surfactant, a brand new capillary tube was used, so as to prevent cross contamination. The capillary tubes, like all other glassware in the experiment, were cleaned thoroughly with deionized water and air dried before coming in contact with any surfactant.

6. Surface Tension Measurements

- Density (Mass/Volume)

Mass measurements were taken on a Metler balance, again, with three digits of accuracy. Afterwards the measured surfactant was poured into a volumetric flask, with two digits of accuracy. The results were placed into a spreadsheet for a resulting density accurate to two decimal places. Three separate weighings and volume measurements were taken.

- Height

Height measurements introduced the greatest amount of error in that the accuracy obtained was barely two digits, very
subjective to the observation point. This was repeated five times for each surfactant, since height was a large factor in the final number obtained for surface tension. Small changes in height values provided significant changes in surface tension, especially since the values for all surfactants were over such a small range.

- Contact Angle

Contact angle was also difficult to measure. Lines were drawn into the captured images of the outer menisci, and a protractor provided the angle. Trigonometry was also used to calculate the angles as a second method to improve the accuracy of the measurement. Three trials were performed: one on each side of the capillary tube using the drawn lines and protractor, and one using trigonometry. Accuracy was again to two decimal places.

In uncertainty analysis, the total uncertainty \( U \) is obtained from the components bias limit \( B \), and precision limit \( P \) by the following relationship:

\[
B^2 + P^2 = U^2
\]

Equation 6.1 - Uncertainty Limit

Bias limit is an estimated measure of the inherent fixed error, which remains constant throughout the data acquisition. This limit is determined by
calibration tests on equipment both before and after the experiment. Bias limit can also be found by combining estimates of system elemental bias errors that have influenced the measurement of the respective variables. Bias limit for the present work includes contributions from system irregularities in the firing mechanism (in the computer), temperature of the lab at the time of testing (on average 25°C), and the number of nozzles suitable for firing in the modules.

Precision limit is an estimate of the unsteadiness or randomness of the experiment. It estimates the lack of repeatability within the experiment. This is the more frequent limit in the present work. General irregularities in the surfactant solution potentially cause the ejected droplets to have irregular properties. To alleviate this, the ejection is recorded on videocassette for at least five minutes while firing and an average behavior is attainable.
7. **Conclusion and Future Research Needs**

For the most part the results correlated with the expected outcome. The trends that were experimentally determined are listed below.

As concentration of surfactant increased:

- Contact angle decreased
- Change in height due to capillarity decreased
- Surface tension decreased
- On average, drop size increased
- Potential for image quality defects increased
- Frequency of ingestion increased

These trends held for both ethylene glycol dimethacrylate and sodium laurel sulfate surfactants. Very different concentrations of each surfactant achieved similar results for surface tension. Specifically, the 0.50% concentration of sodium lauryl sulfate yielded a surface tension of 0.02312 N/m, while the surface tension of 0.02138 N/m was calculated with the 15% ethylene glycol dimethacrylate surfactant. The behavior of the two can be broadly classified as being similar in that they both behaved well when they did in fact fire. They both had problems with ingestion. Thus can be concluded that given this behavior and its repeatability for both surfactants, surface tension lower than 0.023 N/m in inkjet applications is not acceptable.
due to the impacts of ingestion. This inherent problem at surface tensions lower than 0.023 N/m is an issue for image quality in that clogged nozzles cause print defects such as deletions (white spaces), or streaks (white lines) on a print.

Good correlation was found between the behavior of the ethylene glycol dimethacrylate 8.6% surfactant and the commercial grade ink. Looking at the behavior alone, the similarities throughout different stages of droplet ejection and trajectory suggest that the two are very similar in surface tension. Referring to the table surface tension values obtained by the capillary method (Table 5.2), the values are actually only 0.00049 N/m different from one another. Since the behavior of the ethylene glycol concentration and the commercial grade ink is so consistently favorable, the present work finds that ethylene glycol dimethacrylate contains the optimal properties from a ink ejection standpoint with this printhead configuration.

The chart below (7.1) summarizes the results from the observation of the droplet behavior. Here it can been seen that ethylene glycol dimethacrylate 8.6% had the best behavior with respect to geometry, favorable consistency, and the potential effect on image quality. This was most closely related to the ink sample, which had only slightly lower scaled ratings.
A likely reason for the inferior behavior of the commercial ink sample is that the optimization of other ink properties (those other than surface tension) has caused a slight degradation in the ink's behavior characteristics. This, again, is part of a balance that must be obtained during design of the ink.

Reinforcing the point that other factors besides surface tension must be balanced in ink optimization, this chart brings to attention the fact that ethylene glycol dimethacrylate 1% and sodium lauryl sulfate 0.15% have very dissimilar behaviors, despite the fact, recall, that the two have very similar values for surface tension (35.6 and 34.9mN/m, respectively).
**Effect of SLS Concentration on Contact Angle and Capillary Height Change**

![Graph showing the relationship between surfactant concentration and contact angle/capillary height change.](image)

**Chart 7.2 - Contact Angle and Capillary Height Change for SLS**

This chart shows the correlation between capillary height change and contact angle. The first data point at 0.0% concentration gives values for deionized water. Beginning at 0.05% concentration, contact angle and capillary height change have essentially the same relationship with respect to surfactant concentration of sodium laurel sulfate. Both qualities decrease with increasing surfactant concentration. This relationship of surfactant concentration to contact angle to capillary height change holds for ethylene glycol dimethacrylate as well. This is shown in Chart 7.3.
Effect of EG Concentration on Contact Angle and Capillary Height Change

Again, the first value at 0.0% concentration is the values of deionized water. The slight deviation in the uniformity of the relationship between the contact angle and the capillary height change is likely due to the errors discussed in the previous chapter. Surface tension as a function of concentration of surfactant is shown next, along with its relationship to the contact angle. Charts 7.4 and 7.5 which follow show each surfactant's relationship to contact angle.
Surface Tension of Ethylene Glycol Dimethacrylate

![Graph 7.4: Surface Tension and Contact Angle Relationship with SLS](image)

Chart 7.4 - Surface Tension and Contact Angle Relationship with SLS

Surface Tension of Sodium Lauryl Sulfate

![Graph 7.5: Surface Tension and Contact Angle Relationship with EGD](image)

Chart 7.5 - Surface Tension and Contact Angle Relationship with EGD
From these relationships, it can be concluded that as surfactant concentration increases, contact angle, capillary height change, and surface tension decrease. With respect to print or image quality, an optimal ink formulation depends on much more than just the property of surface tension, despite the fact that surface tension is quite important to ejection and behavior of the ink.

Future research needs include a study of what other properties must be optimized individually in order to obtain the best performance ink. Also, the interactions between the properties would be a valuable research topic. Future work could include a quantitative analysis of the droplet size or volume with respect to surfactant and concentration, as well as a quantitative analysis of the recoil distance after the droplet breaks free from the nozzle face with respect to the same factors.

Further, the experiments done in the present work could be done using different surfactants, including standard ethylene glycol dimethacrylate, in order to determine the effect on surface tension and droplet behavior.
8. References


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A1. Droplet Formation

Ethylene Glycol 1%

![Figure AA1.1 - EG 1% Droplet Formation](image)

A. Geometry

The droplet formed by the ejection of ethylene glycol 1% shows a good geometry in the first two pictures. The droplet diameter is even all the way around. Droplets in the first two pictures show a good spherical shape, and the beginning of the 'necking' stage can be seen. Necking occurs right before the droplet pinches off and is free from the nozzle ejection face. The droplet in the last picture does not show good characteristics in that it seems to have excess liquid attached to it. The reason for this will be discussed.

B. Consistency

The good behavior shown in the first two frames above unfortunately was not consistent across all nozzles using the ethylene glycol 1% surfactant. The last of the three pictures above shows a problematic nozzle. This misfire is discussed as an interference effect.

C. Interference Effects
The third picture shows what will be referred to in this paper as an array fire. Sometimes small particles enter and become stuck in the small exit nozzle openings. The particle creates an obstruction that either blocks or interferes with the droplet formation. In this case, the nozzle is only partially blocked, and as a result, two ‘streams’ are formed, one behind the other. Neither droplet is in focus, despite the fact that neighbor nozzles were all in focus, which indicates that both streams of droplets are affected in their directionality by this obstruction.

D. Effect of Surface Tension

For the better behaving nozzles, the effect of surface tension for this surfactant is that surface tension is low enough that the liquid is pushed out of the nozzle, rather than resisting formation out of the nozzle. The meniscus of the surfactant at the air interface of the nozzle stretches to allow the formation of the droplet. The subsequent necking and pinching off of the droplet is due to the surface tension being high enough. Thus, there is a delicate balance with respect to controlling surface tension in inks.

E. Potential Effects on Print Quality

From the first two pictures it can be deduced that recoil will occur shortly after the droplets depart the nozzle. This is favorable from an image quality standpoint once the droplet hits the paper. The interference effect seen in the last picture, on the other hand, is an
unfavorable result for print quality, since directionality of the droplet is hindered by the particle. Droplet misdirectionality causes speckle, deletions (white spaces where there should be ink), ragginess (crooked lines and edges), and decreased sharpness.

F. Non-Surfactant Related Problems Seen

Notable is the fact that interference effects are more a function of the nozzle than the surfactant. Particles may enter the liquid and because the nozzle diameter is so small, any small particle that enters the system has a good chance of becoming an obstruction. It is worth mentioning this report, however, because sometimes surfactants add to the propensity of an obstruction occurring, particularly the higher surface tension surfactants. Higher surface tension surfactants have more difficulty negotiating around particles, and thus the interference effect is exaggerated in such cases.
Ethylene Glycol 5%

Figure AA1.2 - EG 5% Droplet Formation

A. Geometry

Contrary to the droplet formation of ethylene glycol 1%, the 5% surfactant experienced problems with droplet formation. Droplet formation was elongated, with little discernable spherical geometry in the first picture. In the second picture, there is excess liquid seen below the droplet, and the main portion of the droplet is also having trouble achieving a spherical geometry.

B. Consistency

As can be seen looking across the three nozzles pictured above, consistency is not a strength with this surfactant. Consistency is important in predicting the trajectory and behavior of the droplets, and here, three nozzles are showing three different formations.

C. Interference Effects

As will later be discussed, some of the formation difficulty for this surfactant came from the residual ink on the surface of the nozzles. This is a different type of interference than that discussed with
ethylene glycol 1% earlier. This is an interference on the outside of the nozzle in the form of liquid, whereas the 1% surfactant experienced interference on the inside of the nozzle and in the form of a solid particle.

D. Effect of Surface Tension

The role that surface tension plays in the formation of ethylene glycol 5% is that again, the surface tension is low enough that the surfactant does not get trapped in the nozzle, but yet not low enough to allow the droplet to break off when it needs to in order to form an acceptable droplet. Also due to high surface tension is the surface liquid effect seen in the last picture. Again, this will be addressed in a later section.

E. Potential Effects on Print Quality

There are many print quality issues that are affected by this behavior. Residual ink on the surface of the nozzle potentially causes misdirectionality and/or splatter on the page. The lack of consistency is poor for image quality in that unpredictable trajectories and timing need to be controlled.

F. Non-surfactant related problems seen

It is unclear by these pictures alone to discern whether any additional effects are causing problems. It seems that most of the issues exhibited in the testing of this surfactant are due to the surfactant itself.
Ethylene Glycol 8.6%

Figure AA1.3 - EG 8.6% Droplet Formation

A. Geometry

Droplet formation for the EG 8.6% showed good characteristics. Although the droplets were smaller in size than those of other surfactant, their geometry is quite favorable. Various stages in the formation of the droplet can be seen in these pictures. The top far right shows the earliest stages of formation, as the droplet meniscus is stretched out of the nozzle. The top left droplet in the series shows the beginning stages of necking. This stage is very important in formation because it governs the size and geometry of the droplet. Ideally this necking should occur so that the droplet is perfectly spherical. The bottom left-most nozzle shows a droplet after departure from the nozzle face, which is the topic of the section after this one on droplet formation.

B. Consistency
The bottom row of nozzles in the pictures shows the consistency of this behavior with respect to formation size and geometry. The consistency of the droplets was a somewhat expected outcome, since this concentration of surfactant was developed on the basis of O'Horo, et. al.'s published work (1995). What is not consistent, however, and is a weakness of most ink jet applications, is the timing of the drops. All of the above shown nozzles were fired at the exact same time. The cause of this timing issue is interference effects. Ink properties are chosen to minimize, among other things, this inconsistent drop development.

C. Interference Effects
Interference effects are, as described above, result in the mistiming. Inconsistencies and impurities in the surfactant or artifacts in the nozzle cause build up, residue, or imperfections in the nozzles and thus affect nozzle ejection timing.

D. Effect of Surface Tension
Surface tension is a critical player in the behavior of this surfactant. A low enough surface tension allows the meniscus in the nozzle to stretch outside of the nozzle. If surface tension is too high, the surfactant will be unable to leave the nozzle due to the 'skin' around the droplet acting as a barrier. However, if the surface tension of this surfactant were to be too low, there would be no end to the stretching of the meniscus and thus no 'pinch' to form
the droplet. Surface tension may also be responsible in part for the uneven firing times, since higher surface tension would cause the liquid to cling to the artifact, rather than continue through the nozzle.

E. Potential Effects on Print Quality

For the most part, the favorable behavior of this surfactant will result in better print quality than ink containing the other surfactants discussed so far. Small, spherical drops are desirable in ink jet applications. The only source of potential print quality problems might be the firing delays due to artifacts or impurities at the nozzle. Firing timing is important in that as the print cartridge on an ink jet printer moves side to side, the drops are timed to fire such that drops go where the image is being generated. If there is an interruption of this timing, drops will be misplaced on the image.

F. Non-Surfactant Related Problems Seen

Problems besides those related to surface tension were not really found using this surfactant.
Ethylene Glycol 15%

Figure AA1.4 - EG 15% Droplet Formation

A. Geometry

Ethylene glycol 15% showed good geometry characteristics. On the left is seen the earliest stage of droplet formation. The liquid meniscus is stretching to form the beginning of the droplet. The image above on the right shows that the necking occurs as the droplet reaches its full size (when the droplet was about one diameter all around). Here, the spherical shape of the droplet is seen. This surfactant in this respect behaved much like the 8.6% ethylene glycol.

B. Consistency

With respect to drop repeatability, this ethylene glycol 15% behaved well. Observing firing consistency, however, this surfactant did not behave as well as ethylene glycol 8.6%. One of the key observations while using this surfactant that is not really reflected in the pictures is the fact that for this surfactant, ejection was more of an issue. Along the ejection surface, there were isolated nozzles ejecting, rather than just about every nozzle as with 8.6% ethylene glycol. The interference effects were high and are described next.

APPENDIX, 12
C. Interference Effects

The higher concentrations of ethylene glycol tended to have problems with nozzle ejections. This interference is due to difficulties of the meniscus stretching out of the nozzle exit, and can be attributed to surface tension effects described next.

D. Effect of Surface Tension

Surface tension was such that ejection out of the nozzle was symmetric and relatively consistent with respect to geometry. Surface tension is responsible for the inconsistent firing of the nozzles, though. An explanation is that the surface tension for this surfactant was low enough to allow for the tendency of air bubbles to occur in the solution. Even small air bubbles in the solution can easily clog the nozzles, resulting in a lower frequency of fired nozzles.

E. Potential Effects on Print Quality

Print quality is affected by this in that nozzles need to fire consistently and as required. Failure to do so results in white spaces, or deletions. Clogged nozzles affect print density, in that a certain number of drops per inch (dpi) is required to achieve a certain opacity. This dpi value may vary from printer to printer, but clogged nozzles affect the control the printer has over the number of drops put down.

F. Non-Surfactant Related Problems Seen
The issues related to clogged nozzles are more than likely reserved to imperfections in the surfactant, and not related to the nozzle or any other non-surfactant issues.
Sodium Lauryl Sulfate 0.05%

Figure AA1.5 - SLS 0.05% Droplet Formation

A. Geometry

Sodium lauryl sulfate 0.05%, when ejected out of the nozzles, never forms a droplet. Instead what occurs is a stream of liquid with a very uneven geometry, and a very poor consistency rate. This is seen in both images above. The left picture has slightly discernable droplets found in the middle of the stream of liquid. They are joined together by that stream, though, forming a continuum of liquid, rather than distinct droplets.

B. Consistency

This streaming effect occurred more than 90% of the time. In that respect the behavior was consistent. The specific shape, length, and volume of the streams, however, varied greatly from nozzle to nozzle and among firings.

C. Interference Effects

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The problems encountered with this surfactant are not due to interference effects, but entirely due to the surface tension of the surfactant.

D. Effect of Surface Tension

The surface tension of sodium lauryl sulfate 0.05% as shown by these pictures is extremely low. The meniscus is extremely weak, so once a nozzle is fired, liquid continues to stream out of the nozzle, causing a geometry shown above. There is not enough surface tension for the 'necking' to begin as seen with the droplet formation of the ethylene glycol surfactant concentrations.

E. Potential Effects on Print Quality

This type of low surface tension surfactant is the worst case for print quality. Uncontrolled amounts of ink hit a page and form inaccurate images while also increasing the likelihood of smearing due to an excessive amount of ink in one particular place. By these observations, sodium lauryl sulfate in this concentration would not be a recommended surfactant for ink formulation.

F. Non-Surfactant Related Problems Seen

Again, the problems with using sodium lauryl sulfate are due mostly to the surfactant itself. Capturing the droplet ejection in its early stage (as it is just escaping the nozzle) was difficult. The stream of liquid exits the nozzle with the same timing as a small droplet of ethylene glycol, thus making it extremely difficult to image capture.
the beginnings of the liquid stream before the point shown above. However, what is shown above is still part of the droplet formation in that the stream has still not separated itself from the nozzle face, thus in a sense the droplet at this point is still in its formation stage.
Sodium Lauryl Sulfate 0.15%

Figure AA1.6 - SLS 0.15% Droplet Formation

A. Geometry

Coming out of the nozzle, this surfactant looks like it has the potential to form a clean, spherical droplet. However, once the majority of the droplet is out of the nozzle, there is no 'pinching' of the droplet and thus an oblong shape instead of a sphere. The eventual geometry is similar to that of the 0.05% concentration of sodium lauryl sulfate. The difference here is that images were attainable in the earliest stages of formation.

B. Consistency

This behavior was like sodium lauryl sulfate 0.05% in that it was consistent in its poor behavior, but not in the shape and timing of each droplet ejected. From nozzle to nozzle there was also variation. Pinching occurred at varying times due to varying amounts of surfactant leaving the nozzle at each firing.

C. Interference Effects

In the images above, a thin film of liquid was on the nozzle face. This caused some interference, but the behavior of the droplet
formation was not much affected by this interference. The effect of surface interference will be discussed in more detail in a later section.

D. Effect of Surface Tension

A similar problem occurs with sodium lauryl sulfate 0.15% as with 0.05%. Low surface tension causes inconsistent and poorly shaped droplets. The effects from surface tension seemed to be somewhat improved, however, in that formation was observable, as opposed to sodium lauryl sulfate 0.05%, which was difficult to capture at the point of exit. Surface tension was too low in both cases, however, to cause the necking needing to form a favorable droplet eventually.

E. Potential Effects on Print Quality

Print quality for an ink using this surfactant would be affected by the oversized droplet. Surfactants with surface tension as low as this concentration of sodium lauryl sulfate produce unfavorable results. Low surface tension makes droplets difficult to predict, as well. If the pinch off point of the droplet cannot be predicted, it is unlikely that a surfactant of this concentration would be used in an ink.

F. Non-Surfactant Related Problems Seen

Interesting in observing the images above is the fact that the droplets seem to be angled from the vertical. This is most likely
due to air currents in the lab at the time of testing. Though efforts were made to minimize such effects, they are still found in some of the images taken during testing.
Sodium Lauryl Sulfate 0.50%

Figure AA1.7 - SLS 0.50% Droplet Formation

A. Geometry

Preliminary observations of sodium lauryl sulfate 0.05% show acceptable formation behavior. Contrary to the other two concentrations of sodium lauryl sulfate, the 0.50% surfactant had a spherical shape at formation, with necking occurring when the droplet was one diameter all around.

B. Consistency

Of the nozzles that did fire when prompted, the behavior was surprisingly consistent. This was unexpected due to the behavior observed with the other two concentrations of sodium lauryl sulfate. Unfortunately not many of the nozzles did fire with this surfactant.

C. Interference Effects

A saturation level may have been exceeded with the solution used here, creating uneven pockets of surfactant concentration. Much difficulty due to clogged nozzles was encountered while attempting to study this surfactant. Nozzles would clog and not clear as quickly as with other surfactants which experienced this problem.
D. Effect of Surface Tension

Judging by the image above only, the effects of surface tension are favorable, with necking actually taking place with this surfactant (as opposed to the other concentrations). However, this necking occurs late, judging by the size of this droplet in comparison to that of, for example, ethylene glycol 8.6%. The droplet is likely oversized due to the much lower surface tension.

E. Potential Effects on Print Quality

Clogged nozzles are a problem for print quality, as are oversized droplets. Though this droplet is somewhat spherical, its increased size would tend to reduce the amount of resolution attainable by an ink that contains this surfactant. Oversized droplets also take longer to dry on media than smaller droplets. Long dry times increase the chance of smearing of the image.

F. Non-Surfactant Related Problems Seen

The difficulty of making judgement on this surfactant is that this surfactant did not perform well in the conditions of the nozzle, and as a result, obtaining pictures of this concentration was difficult. Much of the information for the discussion above is derived from direct observation of the surfactant. Nozzles clogged so frequently that by the time the camera found and focused on a functioning nozzle, it would already be ceased firing.

Commercial Ink Sample
Figure AA1.8 - Commercial Ink Droplet Formation

A. Geometry

The commercial ink sample initially showed properties similar to those of ethylene glycol 8.6%. Ink is pushed from the nozzle and forms a small droplet head, as seen in the first picture in the series above. The second frame shows a severe necking in which the length of the droplet tail is actually longer than the body of the droplet itself. The last frame shows that this geometry is common for this surfactant. In the middle and right pictures, the droplet itself is slightly oblong, suggesting that once the neck breaks off and recoils into the droplet, a spherical droplet will be formed.

B. Consistency

This long neck effect appeared repeatedly, suggesting that it may have been intentional in the design of the ink. Also consistent with the commercial grade ink was drop size and formation shape.

C. Interference Effects

There did not seem to be any interference effects with this surfactant.

D. Effect of Surface Tension

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From this long neck found in the last picture, it might be concluded that this commercial sample has a slightly lower surface tension than the ethylene glycol 8.6%. Recall that necking during ethylene glycol 8.6% formation occurred when the droplet was one diameter all around, and showed signs of near release at a short distance from the nozzle ejection face. Here, the droplet is a longer distance away from the nozzle face, and the neck is much longer than the ethylene glycol 8.6%. Therefore, by observation alone, one would tend to conclude that the forces of surface tension for this commercial ink sample are lower.

E. Potential Effects on Print Quality

It is difficult to determine what effect this behavior might have on print quality. If the droplet tail recoils into the main body of the droplet and a spherical droplet with no tail is the result, print quality will be favorably affected. If the long neck becomes a tail, as well as if the oblong shape of the droplet seen in the images above, the effect on print quality will be detrimental.

F. Non-Surfactant Related Problems Seen

There may have been a slight air current again in the lab at the time of study for this surfactant which caused the droplet angle from the vertical
A2. Droplet Shape at Departure

Ethylene Glycol 1%

Figure AA2.1 - EG 1% Shape at Departure

A. Geometry

The first of the two pictures above shows the moment just after the droplet has been 'pinched' off from the nozzle. The tail of the droplet is still largely evident, and it is the behavior of this tail that will later govern the droplet's effect on print quality. Looking at the larger part of the droplet mass, the droplet is largely spherical. This lends itself to the idea that the small mass of the tail will easily be incorporated into the larger mass of the droplet itself. The second image is the array fire mentioned earlier. The arrow points to one single droplet that did manage to form a spherical droplet at departure from the nozzle exit.

B. Consistency

The nozzles besides the one shown on the right (the array fire) behaved consistently in their shape at departure. All showed the
same tail that resulted from the neck and pinch of the ejection process.

C. Interference Effects

An interference effect is seen in the second picture. It is an array fire that results in several streams of liquid leaving the nozzle instead of one droplet.

D. Effect of Surface Tension

Surface tension causes the trailing liquid effect seen in the first picture. Surface tension forces would need to pull the tail into the droplet forming the sphere necessary for print quality. In the case of ethylene glycol 1%, the tail of the droplet does in fact get pulled by surface tension into the main body of the droplet. With regard to the array fire, a higher surface tension surfactant than ethylene glycol 1% would tend to clog the nozzle. This surfactant has low enough surface tension to pass through the nozzle despite the interference.

E. Potential Effects on Print Quality

The array fire as discussed next is a problem for print quality. The array fire interferes with print quality in that even a spherical droplet will experience misdirectionality.

F. Non-Surfactant Related Problems Seen

The second frame in the above pictures again shows an array fire, where the one nozzle is creating several streams of droplets. More
clearly in focus in this picture, and indicated by the black arrow, the one droplet fully formed shows that at this given distance from the nozzle opening, there is indeed recoil and a spherical droplet is formed. Unfortunately, the array fire itself interferes with print quality, and even a spherical bubble in this case will experience misdirectionality.
Ethylene Glycol 5%

Figure AA2.2 - EG 5% Shape at Departure

A. Geometry
Looking at all three of these snapshots, it is apparent that the low surface tension of this surfactant has an adverse affect on droplet shape at departure. All three frames show an oblong shape, as well as an inconsistency of droplet size.

B. Consistency
Droplet size inconsistencies are common because the necking and pinch do not occur as they should to regulate the size of the droplet. The three images above show the inconsistency between just three nozzles.

C. Interference Effects
 Aside from small amounts of liquid on the surface of the nozzles as seen in the middle picture, there was little interference.

D. Effect of Surface Tension
Again, necking and pinching do not occur where they should due to the surface tension in this case not being optimal for this nozzle
geometry. Higher surface tension forces tend to pull the droplet into its tightest spherical shape, while droplets with lower surface tension tend to stay odd shaped or oscillate between different shapes.

E. Potential Effects on Print Quality

Inconsistent drop size and geometry are the biggest issues by observation of this surfactant. Inconsistent drop size potentially affects print density, as mentioned earlier. Oblong shapes affect directionality, since the center of mass is displaced from that of a well-formed droplet.

F. Non-Surfactant Related Problems Seen

Focus and lighting with this surfactant were troublesome. The oblong shapes of the droplets affected directionality early in the droplet trajectory, and thus affected the distance from the microscope and camera observing the images. Keeping the droplet at the focal length of the microscope proved difficult for this concentration of ethylene glycol.
Ethylene Glycol 8.6%

Figure AA2.3 - EG 8.6% Shape at Departure

A. Geometry

As with the formation stages, ethylene glycol performed very well at the departure stage. Consistent with the commercial ink sample droplet formation pictures, this ethylene glycol surfactant had good symmetric droplets with a small tail just below the pinch point. Drop geometry was symmetrical in the vertical plane, tail lengths were close to one diameter long, and the two neighboring nozzles showed similar characteristics.

B. Consistency

The droplets are similar in size and geometry, and these two are indicative of the remainder of the nozzle ejections, which had similar results as shown here with only minor and occasional differences. The tail seen in both images consistently occurred in the same place and was of the same length, droplet after droplet and from nozzle to nozzle.

C. Interference Effects
There did not seem to be any interference effects with this surfactant, which is very favorable.

D. Effect of Surface Tension

The surface tension of this concentration of surfactant is similar to that of the commercial grade ink, judging by observation. The surface tension is such that when the droplet is pinched off, both the drop and the tail are consistent in their geometry and size. A lower surface tension ink is difficult to control in this regard. In the case of this surfactant, the forces of gravity and the droplet firing force are controlled by the force of surface tension.

E. Potential Effects on Print Quality

Symmetric drops are easier to control and their trajectory is more predictable. Small droplets enable finer lines and thus higher resolution in print and images. Again, if the tail recoils into the droplet, there are no print defects due to an undersized droplet or a misdirectional tail. It is expected that these droplets of this surfactant will eventually form good droplets, which result in better image quality.

F. Non-Surfactant Related Problems Seen

Nozzle behavior and all non-surfactant conditions were favorable.
Ethylene Glycol 15%

Figure AA2.4 - EG 15% Shape at Deparature

A. Geometry

Ethylene glycol 15% departure droplets behaved somewhat well, though inconsistently. The behavior here was slightly better, though similar to the ethylene glycol 5% surfactant. The first frame shows an oblong droplet with a long tail not directly above the droplet. As this droplet continues its path toward the media, the lightweight tail may find its own trajectory, while the uneven droplet will surely miss its intended target. The second frame shows a better droplet shape at departure, with a slightly oblong droplet and a tail that is more centered over the droplet body. However, looking where the droplet originated, it seems directionality is already an issue. This is a good indication of just how sensitive the droplet trajectory is to the geometry. The last frame is an example of the best case for this surfactant. If there was a tail, it has quickly recoiled and become part of the larger portion of the droplet, and the droplet’s size is favorable in that it is relatively symmetrical.
B. Consistency

The droplet shape at departure was somewhat consistent both from nozzle to nozzle and droplet to droplet. The three images above show three of the most different firings across the nozzle. In other words, what is depicted is essentially a worst case. With that in mind, the latitudes might allow this variation as long as the final result is about the same each firing.

C. Interference Effects

There were no interference effects for ethylene glycol 15%

D. Effect of Surface Tension

The forces of surface tension are responsible for the recoil of the tail as seen in the last image. Surface tension also tends to pull droplets like those pictured in the first two images back into shape. Lower surface tension surfactants keep their tails longer and wobble in their shape over its trajectory.

E. Potential Effects on Print Quality

Having a shape at departure such as that in the right picture is favorable in that by the time the droplet contacts the media below it, a tight, spherical droplet is formed. The other shapes in the left and middle picture have potential to cause problems because their tail are misaligned with the body of the droplet and the tail may go in a different direction than the body.

F. Non-Surfactant Related Problems
There were no problems not related to surfactant for this concentration. At its best, it behaved much like the 8.6% concentration.
Sodium Lauryl Sulfate 0.05%

Figure AA2.5 - SLS 0.05 Shape at Departure

A. Geometry

The shape at departure of sodium lauryl sulfate 0.05% further leads to the conclusion that the surface tension of this concentration is too low. What is seen in both pictures above is a stream of droplets. Most of the time, the droplets stay together and look like one continuous string of liquid as on the left. Other times this stream breaks off into a row of droplets with almost favorable properties as on the right. The size and shape of the droplets in the second frame above are close to acceptable.

B. Consistency

The droplets in the second frame are closer to being acceptable in size and geometry, but each of the three or so droplets shown has a different geometry. Across the nozzles, there is much variation
as is shown simply by these two images. Low surface tension behavior leaves much room for variation.

C. Interference Effects

No interference effects were evident in observing the 0.05% concentration.

D. Effect of Surface Tension

One major problem seen in these images, especially the second, is that although one droplet was fired, three droplets are seen. The same firing frequency was used throughout the experiment and for all surfactants. The fact that three droplets are shown indicates a potential problem with the low surface tension surfactants. Low surface tension surfactants are difficult to keep in the nozzle and limit their outcome.

E. Potential Effects on Print Quality

Using an ink containing surfactant that lowers the surface tension as much as this concentration of sodium lauryl sulfate causes too much ink to be ejected out of the nozzles, and thus too much ink on the media. Thus sodium lauryl sulfate of this concentration would not typically be the surfactant of choice in lowering ink surface tension for ink jet applications.

F. Non-Surfactant Related Problems Seen

Looking at the stream of droplets shown in both pictures, directionality is obviously a concern here. In both cases, the large
stream of liquid is very affected by an air current in the lab. This is because of the amount of surface area that this low surface tension surfactant has. This is as much a function of the surfactant as the air current themselves, but it is worth mentioning as an outside source of problems.
Sodium Lauryl Sulfate 0.15%

Figure AA2.6 - SLS 0.15% Shape at Departure

A. Geometry

The first of the above three frames is the closest to formation of droplets rather than a stream. The first droplet ejected appears to have formed, but the one following has a wide, extended tail behind it. The following two frames show the shape of the ejected droplet, if it can be called that. The stream being ejected has a uniform diameter throughout most its body.

B. Consistency

Drop volume was very inconsistent with sodium lauryl sulfate 0.15%. That it was troublesome was consistent, however, in that the second and third frames in the above series show the repeatability of poor behavior with sodium lauryl sulfate 0.15%. Occasionally a stream would break up into several smaller droplets as is almost the case in the first picture.

C. Interference Effects

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There did not seem to be any interference effects for this surfactant.

D. Effect of Surface Tension

Similar to the 0.05% concentration of sodium lauryl sulfate, the surface tension of SLS 0.15% is too low to produce distinct droplets. Low surface tension surfactants in ink cause inconsistent drop volume. It was difficult to photograph the shape at departure of this surfactant since the ejected stream of liquid was so long. By the time it actually broke from the nozzle exit, the majority of the droplet was out of view, and the next droplet was right behind it in firing.

E. Potential Effects on Print Quality

Drop volume is very important in ink jet applications. The low surface tension surfactants cause high drop volume. Judging from the images above, the volumes of liquid that would potentially contact the media using this concentration of surfactant would completely ruin chances for high image quality. Granted, the nozzles are just microns in size, but the cumulative effect of many nozzles firing as these two are would be quite detrimental to the final product.

F. Non-Surfactant Related Problems Seen

There were no non-surfactant related problems.
A. Geometry

Judging by the image above, the droplet formed using sodium lauryl sulfate has a spherical shape, but is slightly oversized. Looking back at the droplets formed by ethylene glycol 8.6%, the sodium lauryl sulfate surfactant shown here appears to be 1.5 times larger in diameter and volume. The beginning stages of a tail can be seen just above the droplet. This is in contrast to the lower concentrations of sodium lauryl sulfate surfactant, in which the droplets were streams of liquid.

B. Consistency

Though not reflected in the image above, this surfactant was relatively consistent in its production of droplets, rather than streams of liquid. Droplet size did have variation, and at times, an extensive tail would trail the droplet, consistent with lower concentrations of sodium lauryl sulfate. For the most part, however, behavior was more consistently favorable.

C. Interference Effects

Interference effects were not evident while testing this surfactant.
D. Effect of Surface Tension

The surface tension of sodium lauryl sulfate 0.50% is such that at least occasional formation of droplets occurs. The droplets do get ‘pinched’ off, as opposed to the other concentrations of sodium lauryl sulfate. Low surface tension is desirable in that it decreases the amount of energy necessary to eject droplets. But a higher surface tension is needed for this pinching effect. Low surface tension in the case of this surfactant caused major problems with ingestion.

E. Potential Effects on Print Quality

Compared to the other two concentrations of sodium lauryl sulfate, the 0.50% behaved well. The issue with print quality for this surfactant concentration is the oversized drop volume. Resolution is a problem with larger droplet sizes. Currently, most ink jet applications are moving toward smaller and smaller ejection droplets.

F. Non-surfactant related problems seen

This surfactant tended to clog the nozzles at times, so the number of pictures of this surfactant are limited and much of the information discussed with respect to this concentration is based on the videotape of the testing.
Commercial Ink Sample

Figure AA2.8 - Commercial Ink Shape at Departure

A. Geometry

As predicted from the formation pictures of the commercial ink sample, the droplet shape at departure has a distinct tail following it. The two droplets are similar in size and both have a spherical shape. Each droplet's tail is about one diameter in size, as well.

B. Consistency

The fact that this behavior is relatively repeatable is indicated by the two frames. Across the nozzle face, the majority of droplets had the same shape, size, and tail. There was little evidence of any clogging, so the nozzles were all pretty uniform in their ejected droplets.

C. Interference Effects

The shape of the droplet exiting the nozzle at the far right is being affected by surface imperfections, which was discussed in detail in Section 1.3.4.

D. Effect of Surface Tension

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The potential recoil in this situation is an effect attributed to a high enough surface tension. Surface tension governs the size and volume of the droplet, thus making it one of the most important players in ink development. A lower surface tension ink would have more of an oblong shape and a thicker tail. What is shown here is a droplet being acted upon by surface tension, which has pulled the droplet into its spherical shape.

E. Potential Effects on Print Quality

The tail on these droplets shown can cause a shift of the center of mass, which in turn causes misdirectionality. The tails can also become separated and follow their own trajectory, which results in artifacts on the media.

F. Non-surfactant related problems seen

There seems to have been an air current in the lab on the day of testing which caused the droplet trajectory to be angled from the vertical. Materials and test stand used in the data acquisition were chosen such that these effects would be minimized.

APPENDIX, 43
A3. Droplet Imperfections

Ethylene Glycol 1%

Figure AA3.1 - EG 1% Double Droplet with Inconsistent Droplet Size

A. Geometry

Looking at the geometry of the above droplets, there are two droplets. Whether or not they are joined is unclear from the resolution in this image, but regardless, a pinch occurred in the center of the droplet that may or may not have been strong enough to separate the first droplet from the trailing second. The second droplet is also noticeably smaller in size than the first, which lends to the assumption that the second droplet was a follower, not an actual droplet.

B. Consistency

Two important aspects of droplet ejection are consistent droplet size and volume. Ethylene glycol 1% showed signs of problems with both of these requirements. Again, the second droplet is smaller in diameter and volume than the first.

C. Interference Effects

No obvious interference effects were seen with this surfactant.

D. Effect of Surface Tension

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Surface tension is too low in this surfactant to start and stop liquid flow as needed. The first droplet is ejected, and the meniscus at the exit of the nozzle that regulates flow either does not completely form, or forms, but is too weak to withstand the effects of gravity from the next droplet. The liquid that forms the second droplet is typically residual liquid from the nozzle chamber that finds its way out of the nozzle due to the low surface tension conditions.

E. Potential Effects on Print Quality

Since this second droplet is a result of residual liquid, its volume is less than that of a normal droplet, so it does not have any benefit to print quality. Having a droplet like this second one is a detriment to image quality in that it is unaccounted for ink. The satellite droplet can either proceed on its own trajectory, causing an artifact on the print, or it may in some cases catch up to the first droplet and cause a drop volume that is too high. High drop volumes cause image blurring, ink splattering, and ink drying problems.

F. Non-Surfactant Related Problems Seen

The double droplet and inconsistent droplet size seem to be the largest problems faced while using this surfactant.
Ethylene Glycol 5%

Figure AA3.2 - EG 5% Inconsistent Drop Size

A. Geometry

By these images it can be seen that the first droplet actually has a favorable geometry in that it is appropriately sized and spherical in shape. The droplets that trail it, however, decrease in volume and diameter and lose the spherical shape at times. This is somewhat similar to the ethylene glycol 1% in that the secondary droplets follow the first out of the nozzle.

B. Consistency

The two pictures above show two firings of the same nozzle. The multiple droplet fire is a problem consistently, despite the fact that the primary droplet size and volume are consistently favorable. The number and geometry of the trailing droplets behind the primary droplet, however, changes, as seen above, from firing to firing.
C. Interference Effects

The problems just described are due to the behavior of the surfactant itself, and not due to any interference.

D. Effect of Surface Tension

Ethylene glycol 5% presents a similar problem as 1% EG. Surface tension is not high enough to stop residual liquid from falling out of the nozzles in the wake of the first droplet.

E. Potential Effects on Print Quality

It is possible in ink jet printer software to account for this extra drop volume in the programming of their printer drivers, but accurately predicting this behavior is difficult, if possible in some cases at all. Therefore, ink surfactants are optimized for characteristics such as these.

F. Non-Surfactant Related Problems Seen

The nozzle and other non-surfactant components behaved well for this concentration of surfactant.
Ethylene Glycol 8.6%

Figure AA3.3 - EG 8.6% Satellites and Tails

A. Geometry

Again, ethylene glycol 8.6% is exhibiting good behavior in that the imperfections that do emerge using the surfactant are small in magnitude. The first of the three images above shows nearly perfect drop formation. Closer inspection of the area just below the nozzle exit reveals the presence of a satellite, formed either as the main droplet wicked the nozzle surface moisture or as small amounts of the nozzle remains followed the main droplet out. In the second two frames, a tail is evident. The center frame almost looks as though the tail might, at some point in the trajectory, separate from the main droplet and become a satellite. This tail (or potential satellite) is small with respect to the droplet itself, and its impact might be minimal.

B. Consistency

These images show several different nozzles which all seem to be exemplifying the same behavior. A possibility here is that the main drop volume as seen in the second two pictures is just short of the actual needed drop volume. The tail may have been figured to add
the last fraction of volume to complete the droplet that eventually sees the media. If this were the case, and these additions might be able to be accounted for, and thus, consistency would be equally important.

C. Interference Effects

There are no obvious interference effects seen.

D. Effect of Surface Tension

Surface tension in the case of ethylene glycol 8.6% is high enough to pinch the droplet where it should, but not quite high enough to retract that last bit of liquid into the main droplet. There is some tolerance accounted for by this behavior in that if the surface tension of the surfactant is slightly high or slightly low, the droplet response is not very dramatic.

E. Potential Effects on Print Quality

Imperfections of this small magnitude are easily tolerable if they occur on an occasional basis. The drop volume of the satellite is so small that even if it were to follow its own trajectory, its impact would be insignificant and likely invisible to the naked eye. Likewise, if the satellite were to catch up and become one with the main droplet, the increase in volume of the main droplet would not significantly impact print or image quality. If the main droplet is undersized so as to account for satellites and tails catching up to it and adding to its volume, then it is imperative that the tail or
satellite follow the same path and reach the same target at the main droplet.

F. Non-Surfactant Related Problems Seen

The behavior of this surfactant relates the few problems seen here directly to the surfactant itself.
Ethylene Glycol 15%

Figure AA3.4 - EG 15% Satellites

A. Geometry

Ethylene glycol 15% displayed satellites, as well. For the most part, these satellites followed the same trajectory as the main droplet. As for whether the satellites were supplemental or extraneous to the main droplet, it is unclear. These droplets in the two pictures are larger in diameter than those of the lower concentrations of ethylene glycol under the same magnification.

B. Consistency

What is pictured above is two firings of the same nozzle, and the two images are relatively similar in the size of both the primary droplet and the satellite. The spacing between the two seem to be spaced the same distance from one another as well.

C. Interference Effects

There is some liquid on the surface of the nozzle, which can be better seen in the second of the two pictures. However, it is not
likely that the effects seen in the images are due to that small amount of liquid on the nozzle face.

D. Effect of Surface Tension

The increased size of the droplets suggest higher surface tension than the prior discussed surfactants. The droplet needs more mass in order to pinch off and drop from the nozzle to overcome a higher surface tension. Further, when it does actually fall, it tends to pull excess liquid out of the nozzle, which forms the satellite.

E. Potential Effects on Print Quality

The satellites seen here are more significant in size than those seen with ethylene glycol 8.6%, so their effect will be more significant. If these satellites were to catch up and become part of the primary droplet, that droplet would be even more in excess of its favorable size and volume.

F. Non-Surfactant Related Problems Seen

There were no non-surfactant related problems seen.
Sodium Lauryl Sulfate 0.05%

Figure AA3.5 - SLS 0.05% Satellites

A. Geometry

It is easily seen that there are numerous satellites of large volume, to the point that it is unclear at times which droplet is the main droplet. What may have been a stream of liquid at departure has broken up into many droplets.

B. Consistency

This surfactant has had poor properties all the way through the data set, from formation of the droplet to this point. The inconsistency of the droplet size makes it almost impossible for image ejection to be predicted and driven.

C. Interference Effects

Some surface liquid is noticeable in the first image, but it does not seem to be the cause for the problems seen here.

D. Effect of Surface Tension
Based on this surfactant’s behavior in the stages preceding this one, it is not surprising that the lack of surface tension in this surfactant creates problems with satellites and elongated droplets and tails. The stream of liquid ejected from the nozzle gets broken up by air currents and by different momentum of various parts of the stream to become the irregularly shaped droplets seen above.

E. Potential Effects on Print Quality

The lack of definition in these droplets causes a myriad of problems once that much ink contacts the media. Droplets of controlled geometry are essential since their size, shape, and center of mass affects their trajectory.

F. Non-Surfactant Related Problems Seen

The images of sodium lauryl sulfate 0.05% did not come out as well as other surfactants due to difficulties with the camera and lighting at the time of data acquisition. Beyond that issue, there also seems to have been an air current in the room at the time this surfactant was being studies. The air current tended to cause the droplet stream to be angular.
Sodium Lauryl Sulfate 0.15%

Figure AA3.6 - SLS 0.15% Tails, Inconsistent Drop Size

A. Geometry

Looking at the three images above, a geometry can hardly be defined. An initial droplet leaves the nozzle and liquid continues to flow out of the nozzle, affecting while the primary droplet while causing excess liquid to follow in random geometries.

B. Consistency

Again very similar to sodium lauryl sulfate 0.05% is the more concentrated 0.15% surfactant. Many of the same problems occur, as they have all they way through since formation.

C. Interference Effects

The surface liquid seen in the images shows the tendency for liquid to just ‘fall’ out of the nozzles after the firing. Opposite to high surface tension inks which pull the liquid out of the nozzles, low surface tension inks tend to ‘fall’ out of the nozzles due to the
forces of gravity. This excess liquid tends to interfere with the next firing.

D. Effect of Surface Tension

A low surface tension causes a stream of liquid to be ejected out of the nozzle, and the little surface tension that is present causes the stream to start pinching off and forming a number of droplets. Since this is a result of one firing, the expected result is one droplet, not a stream of liquid.

E. Potential Effects on Print Quality

Having this many extraneous droplets makes predicting print outputs close to impossible. Drop volumes are too variant to account for each volume of surfactant.

F. Non-Surfactant Related Problems Seen

All problems with sodium lauryl sulfate 0.15% are due to the surfactant itself.

SLS 0.50%

There are no pictures of satellites, tails, or other imperfections, because they were not observed. This was in part due to the fact that not many of the nozzles fired the surfactant well. Many clogged very often, making it difficult to observe the droplet behavior. Of the limited number of images that were obtained, there were no droplet imperfections found.
Commercial Ink Sample

Figure AA3.7 - Commercial Ink Satellites

A. Geometry

Surprisingly, the commercial ink sample when fired through the nozzles generated many satellites. It is obvious that in this case, the satellites to not follow the trajectory of the main droplet. Droplets are quite spherical and tight. On the other hand, satellites are small but significant in their consistency.

B. Consistency

The shape of the droplets as well as that of the satellites is very consistent. The trajectory of the droplets is also constant. Interestingly enough, the trajectory of the satellites is constant in itself. This is a perfect example of what was mentioned earlier regarding the impact of droplet size and geometry on its path.

C. Interference Effects
The main droplets seem to have been affected by some moisture on the ejection face of the nozzles. This will be discussed in detail later.

D. Effect of Surface Tension

It is unclear whether these satellites are getting pulled by the main droplet out of the nozzle, which would imply high surface tension, or if the satellites are falling out of the nozzle, implying low surface tension. The shape of the droplets themselves implies that the surfactants in this ink have been optimized for main droplet size.

E. Potential Effects on Print Quality

Whatever the reason for the non-vertical path of the droplets, having the satellites in a different path will cause artifacts on the print media. As mentioned before, this type of droplet imperfection is sought to be minimized, but it is rarely eliminated.

F. Non-Surfactant Related Problems Seen

In addition to the interference of the surface droplet, these droplets seem be getting affected by an air current. These images were taken with a lower magnification than those seen earlier so that the effect could be clearly seen across several nozzles.
Commercial Ink, continued

Figure AA3.8 - Commercial Ink Tail

A. Geometry

This droplet of commercial ink did not have the satellites as those in the prior discussion had. It does, however, have a tail, which will later recoil into the droplet. The tail is almost a full diameter long.

B. Consistency

This phenomenon occurred consistently in opposition to satellites. Thus, almost every nozzle ejected a droplet with either a small tail or a small satellite.

C. Interference Effects

There is a thin surface skin on the face of the nozzle which has the potential to affect the droplet ejection and may have done so to some extent in this case. More than likely the surface drop did cause the angle in the droplet's trajectory.

D. Effect of Surface Tension

High surface tension causes the interference effect just mentioned, but low enough surface tension allows the droplet to break free of the larger mass of liquid and fall toward the media. This tail seen
here will later recoil into the larger part of the droplet by the effects of surface tension.

E. Potential Effects on Print Quality

This type of droplet imperfection is tolerable and possibly accounted for in print design. The misdirectionality, however may not be as easily accounted for.

F. Non-Surfactant Related Problems Seen

Problems shown above are due to surface tension, including the misdirectionality. Air currents were not the cause of the angled trajectory, but instead surface droplet interference. See (C) of this section for more details of the surface interference found with this surfactant.
A4. Droplet Recoil

Ethylene Glycol 1%

Figure AA4.1 - EG 1% Recoil

A. Geometry

This droplet has recoiled within two diameters of the nozzle exit. The shape of the droplet is spherical, with no evidence of a tail or satellite which may have been present at ejection. The droplet does look large with respect to the commercial grade ink droplets described later, however.

B. Consistency

Recoil for this surfactant occurred at the same distance from the nozzle for each droplet. Also, the size of the droplet as a result of the recoil was similar among firings.

C. Interference Effects

There were no interference effects with ethylene glycol 1%.

D. Effect of Surface Tension
The distance in which this recoil occurs with respect to the nozzle exit is dependent on the properties of the surfactant. A higher surface tension surfactant would be expected to recoil sooner than one of lower surface tension. A lower surface tension surfactant, on the other hand, such as ethylene glycol 1% would not tend to encounter the problem of rebound as severely because the surface tension is not strong enough to ‘snap’ the droplet into shape, which is what would cause the vibration in the droplet.

E. Potential Effects on Print Quality

The potential effect of this rebound effect is the chance of the droplet hitting the media while in an oblong shape. Thus, if there is not a sufficient gap between the nozzle and the media, the rebound effect of the recoil may not have a chance to dampen out. For this case, even if there is no rebound effect, oversized droplets decrease the amount of resolution attainable by the printer.

F. Non-Surfactant Related Problems Seen

Recoil was exclusively related to the surfactant.
Ethylene Glycol 5%

Figure AA4.2 - EG 5% Perfect Recoil (1), Imperfect Recoil (2)

A. Geometry

These two pictures of ethylene glycol 5% show both perfect and imperfect recoil. This demonstrates that there may be inconsistencies in recoil timing. The first picture is a well-rounded droplet about three diameters away from the ejection surface. The next picture shows a similarly sized droplet still carrying the remains of a tail. This droplet has not yet recoiled, despite the fact that the droplet is more on the order of five diameters away from the nozzle exit. If the intended media is three diameters away, the droplet on the left result in a normal drop on the media, but the droplet on the right may have some imperfections it its vicinity once in contact with the media.

B. Consistency

As seen by the two images above, consistency was a problem for ethylene glycol 5%. Some nozzles ejected droplets that recoiled quickly and cleanly, while others fired droplets that wobbled with visible tails all the way out of the viewing area.
C. Interference Effects

The effects seen are not due to interference. Little if any interference was seen at all.

D. Effect of Surface Tension

Surface tension causes the droplet to snap into place as it has on the left. The forces that give the droplet its shape are the same ones that pull a tail into the main body of the droplet. On the right, there seems to be more of a tail remaining, which implies that the forces were not high enough in this case to make up for the poor shape as yet.

E. Potential Effects on Print Quality

The droplet on the left would be favorable from a print quality sense, since the droplet is well formed early in its trajectory. The droplet on the right, however, still has liquid trailing behind it, seemingly being carried by the droplet. This liquid will contact the media and cause a spray effect.

F. Non-Surfactant Related Problems Seen

The problems discussed above are due to the surfactant itself for the most part. However, it is possible here, as in all the cases earlier, that the ejection nozzle such as that on the right may have accumulated a film or other ‘skin’ on the perimeter of the exit nozzle. This would cause many types of physical problems with
the droplet size and geometry. The effects of surface tension for
the most part tend to counter many of these physical imperfections.
Ethylene Glycol 8.6%

Figure AA4.3 - EG 8.6% Recoil

A. Geometry

The ethylene glycol 8.6% behaved the best out of the EG surfactants, once again. Looking at the two consecutive nozzles pictured above, the size, geometry, and distance from the nozzle are about the same, with no remaining satellites or tails on either. The only slight difference, if any, is the droplet size, and that difference is especially slight compared to what is seen with other surfactants.

B. Consistency

Droplet size consistency is important and is typically held within a given tolerance. The size of these droplets after recoil is very similar, and they were so for each firing.

C. Interference Effects

The surface of the nozzle as well as the nozzle exits seem to be clear of all obstructions or excess liquid.

D. Effect of Surface Tension

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There seems to be a rebound effect occurring in the right picture above, just at the exit of the nozzle. This is likely due to the excess liquid clinging to the ejected droplet for a small fraction of time and then letting the main droplet go. This would likely be seen using higher surface tension surfactants.

E. Potential Effects on Print Quality

That the recoil occurs in the same place and results in the same droplet shape is very good for print quality. A droplet in the process of 'rebounding' after recoil is likely to experience misdirectionality.

These droplets shown above would do well for print quality.

F. Non-Surfactant Related Problems Seen

These surfactant droplets behaved quite well and quite consistently.
A. Geometry

Ethylene glycol 15% behaves much like the 8.6%. From this picture, recoil seems to occur closer to the nozzle exit than with the lower concentration surfactant, but the size and geometry of the droplet shown in this picture seem to be about the same. Again, it is noticeable that there are no satellites or evidence of a tail behind this droplet.

B. Consistency

This effect described above occurred consistently across the nozzles and among firings.

C. Interference Effects

This surfactant tended to clog the nozzles somewhat. Every so often a nozzle would cease to fire. This may be attributed to pockets of non-uniform mixture attempting to exit the nozzles. The interference would eventually clear and the nozzle would fire normally after some time.

D. Effect of Surface Tension
The interference described just above is likely due to areas of higher surface tension (likely areas of higher water content) becoming stuck in the nozzle exit. The interference probably cleared when enough surfactant mixed with the deionized water to lower the surface tension, giving it the opportunity to exit the nozzle. The image above, on the other hand, shows the effect of the droplet ejecting well.

E. Potential Effects on Print Quality

Recoil occurred quickly after release of the droplet for this surfactant. This is desirable, since in the event of a rebound or reverberation effect, the droplet has enough distance left in its trajectory to stabilize before contacting the media.

F. Non-Surfactant Related Problems Seen

The problems seem with this surfactant were in fact surfactant related.
A. Geometry

Looking at the above images, it is difficult to tell if there was any recoil whatsoever, especially in the stream on the right. Where there might be some recoil, as on the left, there are obvious discrepancies in droplet size and geometry.

B. Consistency

Sodium lauryl sulfate 0.05% consistently behaved poorly, as with most other stages of its development. The drop recoil, however, occurred at different distances and resulted in different drop sizes. Each nozzle and each firing produced a different stream of liquid, so recoil virtually never occurred in the same place.

C. Interference Effects
The liquid seen on the exit of the nozzles at the top of both images above is due to low surface tension and is not an interference. Thus there were no interference effects noticed using this concentration of surfactant.

D. Effect of Surface Tension

Again getting back to the low surface tension effects, the droplet ejection has no end, as an entire stream of liquid comes out of the nozzle. Contrary to the higher concentrations of ethylene glycol, the sodium lauryl sulfate 0.05% concentration showed poor recoil properties. What does actually form into smaller droplets often has tails and satellites attached to it, and drop size is quite inconsistent. Low surface tension is the cause of this behavior. Low surface tension also causes the ‘peeking’ of the liquid out of the nozzle exit seen in both images above.

E. Potential Effects on Print Quality

As mentioned in the earlier section, low surface tension is a favorable characteristic for quick dry times, since low surface tension ink gets ‘wicked’ into the media more quickly and thus dries quicker. However, drying is secondary to control of droplet ejection, and surfactants in ink are typically driven by the nozzle specifications (what is best controlled out of the nozzle). It is not surprising, therefore, that recoil is a concern. Controlling the directionality of any or all of these droplets is next to impossible.
F. Non-Surfactant Related Problems Seen

There were no non-surfactant related problems seen.
Sodium Lauryl Sulfate 0.15%

Figure AA4.6 - SLS 0.15% Recoil

A. Geometry

Sodium lauryl sulfate 0.15% showed much improvement over the 0.05% surfactant. The droplet is spherical, with no tails or satellites, and it appears to have recoiled within a short amount of time. The droplet size seems to be a little large compared to that of the ethylene glycol family.

B. Consistency

Though depicted here is a well-recoiled droplet, what was seen equally as often was the effect shown in the images of sodium lauryl sulfate 0.05% described just before this. Thus, consistency was a problem with the 0.15% surfactant.

C. Interference Effects

Interference effects did not play a role in the recoil of these droplets.

D. Effect of Surface Tension
Surface tension in the case of this surfactant was inconsistent.
This may have, like the case of 15% ethylene glycol, been due to irregularities and imperfections in the dilute sodium lauryl solution.
Thus there were inconsistencies in surface tension and thus in droplet performance.

E. Potential Effects on Print Quality

The inconsistency of the droplet recoil relates to the inconsistency of the formation during this testing with sodium lauryl sulfate 0.15%. For the purposes of drop prediction, this surfactant did not produce predicable results, thus designing the software to accommodate a ink jet printer using ink with this surfactant would be extremely difficult.

F. Non-Surfactant Related Problems Seen

The main problem with this surfactant’s recoil properties deal with inconsistencies in its formation. Thus the majority of problems are actually surfactant related.
Sodium Lauryl Sulfate 0.50%

Figure AA4.7 - SLS 0.50% Recoil

A. Geometry

The droplet appears to have formed completely by the time shown. Recoil seems to have taken the same amount of distance as for 0.15%, and the size is about the same.

B. Consistency

This surfactant produced favorable droplets more often than the prior concentration of sodium lauryl sulfate, but still not often enough to be acceptable for ink use.

C. Interference Effects

There were some interference effects in that some of the nozzles were clogged somewhat, but this may have been due to particles or any other type of nozzle interference. This would affect formation, however, and not recoil.

D. Effect of Surface Tension
Inconsistent recoil was observed with this surfactant, but only because ejected droplet geometry varied so much. Surface tension recoiled the droplet when the droplet shape was favorable.

E. Potential Effects on Print Quality

The effects of this inconsistent recoil are similar to that of the above described concentration of surfactant in that inconsistency makes droplets difficult to control.

F. Non-Surfactant Related Problems Seen

Directionality was a bit of an issue with this surfactant, which is the reason the droplet is slightly out of focus. This could have been caused by any number of things, such as impurities in the nozzle, camera focus, or lighting issues.
Commercial Ink Sample

Figure AA4.8 - Commercial Ink Recoil

A. Geometry

The commercial ink sample showed great recoil, with a small drop, no satellites, and no tail. There does not seem at the time of first recoil to be any 'rebound' effect, since the droplet is very symmetrical. Rebound occurs within a short distance of the droplet leaving the nozzle face.

B. Consistency

Despite many factors, including surface liquid and air currents in the lab at the time of testing, these droplets formed consistently.

C. Interference Effects

Shown in the upper right corner of the pictures is a surface bubble, one of the surface defects discussed in the next section. This bubble, however, does not appear to have adversely affected this commercial ink droplet.

D. Effect of Surface Tension
Surface tension in the commercial ink sample is obviously optimized for this application and is apparently robust enough to withstand the adverse conditions it is being fired into.

E. Potential Effects on Print Quality

This persistence of the recoil with the commercial ink sample is very good for print quality in that the latitude designed into this ink allows it to recoil well in many conditions. Surface liquid aside, the software can be programmed to run the printer fairly accurately, at least with respect to the controlling the droplets since these droplets form well so much of the time.

F. Non-Surfactant Related Problems Seen

There were no non-surfactant related problems seen.
A5. Effects of Surface Liquid on Droplets

Ethylene Glycol 1%

![Figure AA5.1 - EG 1% Surface Droplet](image_url)

A. Description of Picture

A similar effect is seen with ethylene glycol 1% as was observed with the commercial grade ink. In the images of the ethylene glycol surfactant above show a surface droplet in between two nozzles. Important to note here is that these are not two consecutive nozzles on each side of the droplet. Rather, there are three nozzles present in the picture - one on each side of the droplet, and one in the center of the droplet that is completely obstructed.

B. Effect of Interference

The center nozzle does not fire at all, while the two outer nozzles fire misdirectionally. Again, the cumulative effect of these three nozzles on the surface droplet is cumulative until the mass of the droplet exceeds the amount of surface tension forces holding it to the module edge. Thus this surface droplet affects three
consecutive nozzles while adding a considerable localized amount
...of ink under the droplet.

C. Effect of Surface Tension

Surface tension causes the surface droplets to cling to the nozzle
exit. The droplets actually managing to escape around the surface
droplet are elongated, obviously affected by the high surface
tension that holds the large surface droplet onto the nozzle.

D. Potential Effects on Print Quality

Effects on print quality are similar to those discussed above in that
misdirectionality caused by this large surface droplet affects the
placement of the ejected droplets. The surface droplet being there
itself blocks many nozzles, leaving potential for white spaces on an
image. Lastly, once the weight of the surface droplet exceeds the
force of surface tension holding it on the nozzle face, the droplet
falls to the media, creating an extremely high volume, large size
drop on the image, which is detrimental for all aspects of print
quality.

E. Non-Surfactant Related Problems Seen

Again, focusing both the camera and the microscope was more
difficult due to the surface droplet.
Ethylene Glycol 5%

Figure AA5.2 - EG 5% Surface Liquid

A. Description of picture

Contrary to what was observed with the last two surfactants, ethylene glycol dimethacrylate 5% faced another problem. Present on the module nozzle edge in this case was not a surface droplet, but instead a thin coating of liquid across several nozzle exit areas. Where the mass collection and dropping of a large droplet was not present in this situation, the surface liquid did present problems of its own in addition to being a precursor for a large surface droplet. Pictured above on the right side is an obstructed nozzle.

B. Effect of Interference

The liquid layer, though thin, is enough to divert the fired liquid droplet from its trajectory. The ejected liquid droplet instead remains on the surface across the nozzles, and again, high surface tension is the cause. The nozzle on the left is firing, but with difficulty. The ejected droplet is acquiring excess liquid on its path.

Effect of Surface Tension
The surface tension is low enough that combined with the force of gravity, the droplet falls. However, surface tension is high enough to bind extra liquid to this droplet and cause a higher volume droplet than what is desired.

Potential Effects on Print Quality

Higher drop volumes are poor for resolution. With even desk model ink jet printers boasting 1400 dots per inch, a drop volume as seen above is a major issue.

Non-Surfactant Related Problems Seen

There were no obvious non-surfactant related problems.
Figure AA5.3 - EG 8.6% Ejection from Clogged Nozzle (1), Separation of Misaligned Droplet (2)

Description of Pictures

The two images above are another example of an effect of droplets on the surface of ink jet nozzles. On the right is a 'well-conditioned' nozzle, and the ejecting droplet shows good characteristics, as discussed in earlier sections. On the far left is a surface droplet, obstructing several nozzle exits. At the very edge of this droplet is a nozzle exit, out of which a droplet is forming and subsequently getting drawn in toward the large droplet. The first of the two pictures above shows the point at which this ejected droplet attempts to break away from the surface bubble. It successfully does so, as seen in the second picture.

Effect of Interference
The directionality of this droplet has obviously been adversely affected, and possibly the drop volume. Naturally, the nozzles under which the surface droplet is found are not firing at all and are completely blocked by this surface droplet. This surface droplet has the potential to break off and fall to the media.

Effect of Surface Tension

Surface tension allows the droplet to form on the surface of the nozzles while also allowing the ejected droplet to break free. High enough surface tension keeps the droplet on the nozzle, and low enough surface tension allows it to break off. There is a compromise, therefore.

Potential Effects on Print Quality

The effects on print quality are due to a misdirectional and oversized droplet, as well as clogged nozzles along the length of the ejection face.

Non-Surfactant Related Problems Seen

There were no non-surfactant related problems seen.

Sodium Lauryl Sulfate, all concentrations:

Notice in this section there are no images of surface droplets or liquid effects for sodium lauryl sulfate. It is because none were observed. This is in keeping with predictions, since by all other indications, the sodium lauryl sulfate surfactants displayed the behavior of lower surface tension surfactants. Lower surface

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tension forces do not allow the surfactant to ‘cling’ to the surface of the ejection face.
A. Description of Picture

The above two pictures demonstrate the effect of a surface droplet on the firing of commercial ink. A surface droplet is obstructing the ejection of several nozzles on the nozzle face. The nozzle to the left is unobstructed and the resultant droplet is directionally stable. The right nozzle in both of the above images shows the detrimental effect that surface droplets can have on ink droplets.

B. Effect of Interference

Surface droplets themselves are not a problem so much as the problems that they cause. What is pictured above is a nozzle partially obstructed by a surface droplet. The result of this partial
obstruction is the formation of a droplet with a directionality problem from the start. The droplet finds its way out of the nozzle just around the surface droplet. As a result, it begins a trajectory far from vertical. Further, liquid from the ejection droplet may be lost to the surface droplet, again by the effects of surface tension. In the worst case, all of the ejection droplet is lost to the surface bubble. The result is a local saturation on the surface. Eventually, the volume and mass of the surface bubble become large enough that a significant drop (about a quarter of the size of the surface bubble) falls from the surface bubble.

C. Effect of Surface Tension

The cause of this surface bubble, as well as the one on the left in the lower picture, deals with the surface tension of the surfactants in the ink. A low surface tension ink would not cling to the piezo module the way that these droplets are, but rather would fall right off the edge. In that sense, a high surface tension ink provides this disadvantage - surface droplets.

D. Potential Effects on Print Quality

The high volume of this large drop make controlling print quality a near impossibility. This being seen for the commercial grade ink, it is questionable why such surfactant that causes this result would be used.

E. Non-Surfactant Related Problems Seen

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The left droplet shown in both pictures is slightly out of focus due to the fact that the camera and microscope were primarily focused on the surface bubble and the nozzle on the right side.

One explanation of why the ink shown here behaves in this way is that there are other factors besides surface tension affecting the ejection of this ink. Thus, it is not only the surface tension of the ink that drives this property but possibly other factors, such as properties of the nozzle surface itself. For example, impurities on the nozzle surface may affect the wettability of that surface and thus increase the likelihood that the liquid would have an affinity toward it. Despite attempts to not handle the module surface, human oils may have gotten on it, affecting its behavior with liquid surfactants.