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**Influence of surface chemistry and electric fields on the
nucleation of ice and hydrates**

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by

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To Vignesh Prakash

No other friend would be as delighted to have a body of knowledge dedicated to him.

You are greatly missed.

“I don’t know if you have had the same experience, but a thing I have found in life is that from time to time, as you jog along, there occur moments which you are able to recognize immediately with the naked eye as high spots. Something tells you that they are going to remain etched, if etched is the word I want, for ever on the memory and will come back to you at intervals down the years, as you are dropping off to sleep, banishing that drowsy feeling and causing you to leap on the pillow like a gaffed salmon.”

P.G. Wodehouse, *The Code of the Woosters*

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Influence of surface chemistry and electric fields on the nucleation of ice and hydrates

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Understanding and controlling the formation of ice and hydrates has important energy-related applications including ice mitigation, methane harvesting from hydrates, and desalination by freezing. This dissertation describes multiple studies to explore the role of surface chemistry and electric fields on the nucleation of ice and hydrates.

The first part of this dissertation describes a study on saltwater ice formation. A majority of the available literature on ice mitigation concerns freshwater icing, unlike this study. This work quantifies the influence of surface chemistry and texture on saltwater ice formation. Two kinds of experiments are conducted as part of this effort. The first set of experiments quantifies the influence of surface chemistry on ice nucleation of various saltwater solutions. It is noted that a large number of individual experiments were conducted, which makes the present results statistically meaningful, unlike most previous studies. The second set of experiments studies the dynamics associated with impact of saltwater droplets on supercooled superhydrophobic surfaces. It is seen that the saltwater droplets retract more than freshwater droplets (after impact). The greater bounciness of saltwater droplets is a result of slower ice

nucleation propagation kinetics. These experiments indicate that superhydrophobic surfaces will offer greater resistance to impact icing with saltwater than pure water and can remain useful at temperatures as low as $-40\text{ }^{\circ}\text{C}$.

The second part of the dissertation includes a detailed study of electrofreezing, i.e., the electrically induced nucleation of ice from supercooled water. This work studies ice nucleation in electrowetted water droplets, wherein there is no electric field inside the droplet resting on a dielectric layer. Instead, there is an interfacial electric field and charge buildup at the solid-liquid interface. Through carefully planned experiments, the influence of electric fields and electric currents on the freezing temperature elevation is quantified. The results facilitate an in-depth understanding of various mechanisms underlying electrofreezing. Firstly, interfacial electric fields alone can significantly elevate freezing temperatures by more than $15\text{ }^{\circ}\text{C}$ in the absence of current flow. Secondly, electrofreezing-induced temperature elevation saturates at high electric field strengths. Thirdly, the polarity of the interfacial charge does not significantly influence electrofreezing. Finally, current flow can further elevate the nucleation temperature by providing additional triggers for nucleation events. Overall, both the electric field and the electric current influence electrofreezing; however, the physical mechanisms are very different.

The third part of the dissertation studies a novel concept to induce rapid formation of hydrates. The long induction times (hours to days) associated with hydrate nucleation is a significant barrier to many hydrate-based applications. The present work shows that electro-nucleation can promote rapid hydrate nucleation. Experiments were conducted with tetrahydrofuran (THF) hydrates, which is a model hydrate used in many studies as a precursor to studies with methane hydrates. The results show that hydrate nucleation can be triggered in less than ten minutes by

applying electro-nucleation voltages. The voltage-induced current flow through the precursor solution leads to bubble generation on the electrodes. These bubbles act as nucleation sites and provide triggers to initiate rapid nucleation. Electro-nucleation is thus seen a powerful technique to induce rapid hydrate nucleation.

In summary, the work conducted in this dissertation significantly advances our current understanding of nucleation and liquid-solid phase change. It also develops and characterizes new tools and concepts to stimulate and control nucleation. Therefore, in addition to the fundamental contributions in the field of phase change, this work can enable the development of new energy-relevant applications.

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Chapter 1

Introduction and literature survey

Solid-liquid phase transitions are ubiquitous, with one of the most familiar transitions being the freezing of water to ice. The ability to control or predict ice nucleation influences a variety of applications. Within these wide-ranging applications, there are applications that require either the promotion or the suppression of ice nucleation.

Unwanted ice formation has negative efficiency and safety consequences for the aviation, energy, and infrastructure sectors. Many anti-icing methods use active techniques, which require supplying thermal or mechanical energy, and thus involve high costs or complexity [1]. Among passive techniques, it has clearly been observed that low surface energy translates to icephobicity, i.e., delayed ice nucleation and/or lower ice adhesion strength. Consequently, there have been numerous R&D efforts on the analysis and development of surfaces to suppress ice nucleation (i.e., creating icephobic surfaces) [1–5]. It is noted that most of these applications and studies involve ice formation with freshwater.

Saltwater icing poses significant engineering challenges; however, saltwater ice mitigation is not as well studied as freshwater ice mitigation. Saltwater ice formation on offshore oil-gas platforms, ships, and any marine structures can cause a vast array of structural and safety problems, as shown in Figures 1.1(a) and 1.1(b). In particular, bow spray, which occurs when seawater is displaced by the movement of the bow and lands on the structure, can create stability problems when the seawater freezes

asymmetrically and above the center of gravity [6]. Furthermore, ice formation can damage structural components, cause slip hazards, and damage/disable equipment [6]. Moreover, the ice extent in the Arctic is slowly decreasing [7], which implies greater transportation and oil-gas drilling activity in Arctic regions. The negative effects of saltwater icing are expected to become more severe in the future.

Desalination via freezing is another promising application (Figure 1.1(d)), which would benefit from promotion of ice nucleation. Of the 1.4 billion km^3 of water worldwide, only 0.5% is accessible fresh water [8]. Furthermore, with a projected population growth of 40-50% and the associated increased industrialization and urbanization, the demand for available water resources will substantially increase [9]. Desalination via freezing consumes less energy than thermal desalination because the latent heat of vaporization is 2261 kJ/kg, whereas the latent heat of freezing is only 334 kJ/kg [10].

In addition to ice, another significant application where nucleation suppression is critical concerns methane hydrate formation in oil and gas pipelines (i.e., flow assurance). Hydrates are clathrate structures consisting of a guest molecule (e.g., methane, carbon dioxide, ethane, propane, hydrogen sulphide, etc.) trapped in a lattice of water molecules (Figure 1.2(a)). Visually, methane hydrates resemble ice and form under high pressure, low temperature conditions in a water and methane environment (Figure 1.2(b)). However, they are flammable and are therefore referred to as ‘ice that burns’.

Globally, the oil and gas industry is expanding deepwater production; however, the operating conditions (high pressure, low temperature) in subsea infrastructures favor natural gas hydrate formation. When formed in pipelines, hydrates plug the transmission lines (Figure 1.2(b)), which halts production until the hydrates dissoci-

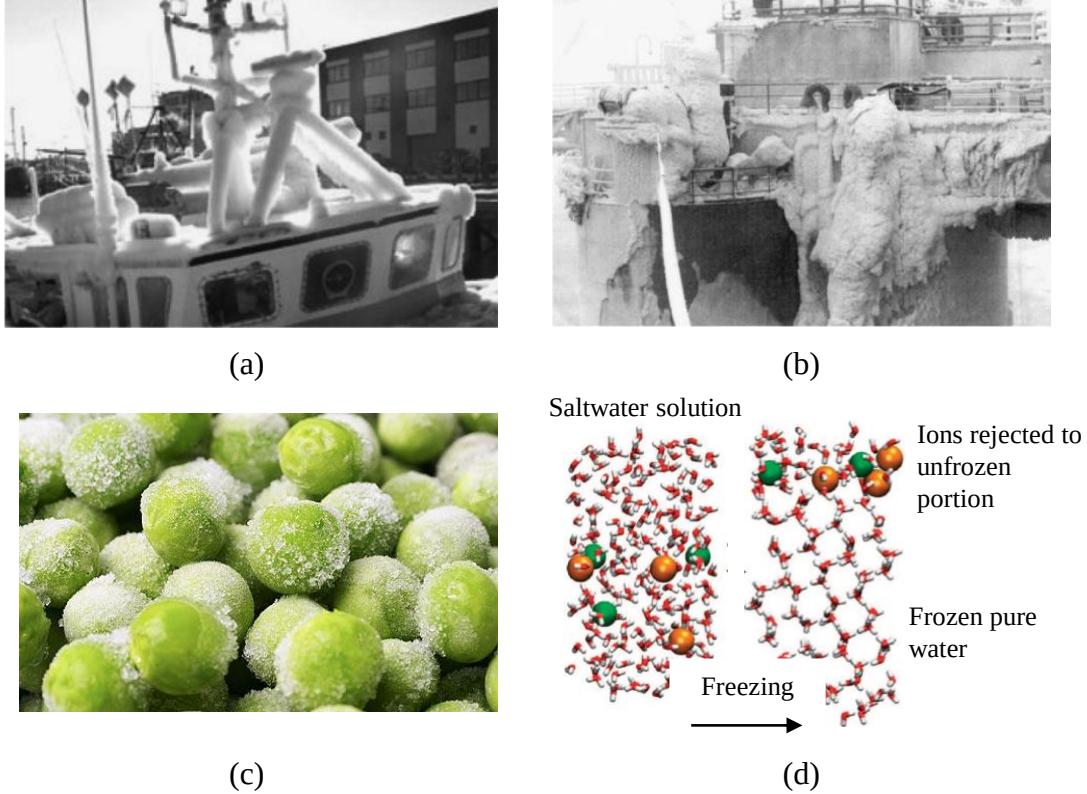


Figure 1.1. Applications where a study of saltwater icing is critical a) marine vessels [6], b) offshore oil-gas platforms [6], c) food preservation [11], and d) freezing desalination (reprinted with permission from [12]).

ate, which could take months [14]. This is also a severe safety risk; when hydrates detach from a pipeline wall, the high-pressure condition can rapidly push the hydrates through the pipeline (300 km/hr), leading to pipeline rupture and blowouts [14]. To prevent hydrate formation, costly and/or environmentally unfriendly thermodynamic inhibitors and kinetic inhibitors (e.g., methanol) are commonly used [15]. It is estimated that US\$220 million is spent annually on methanol to prevent hydrate formation [14].

While the goal of the aforementioned applications is to prevent or delay nu-

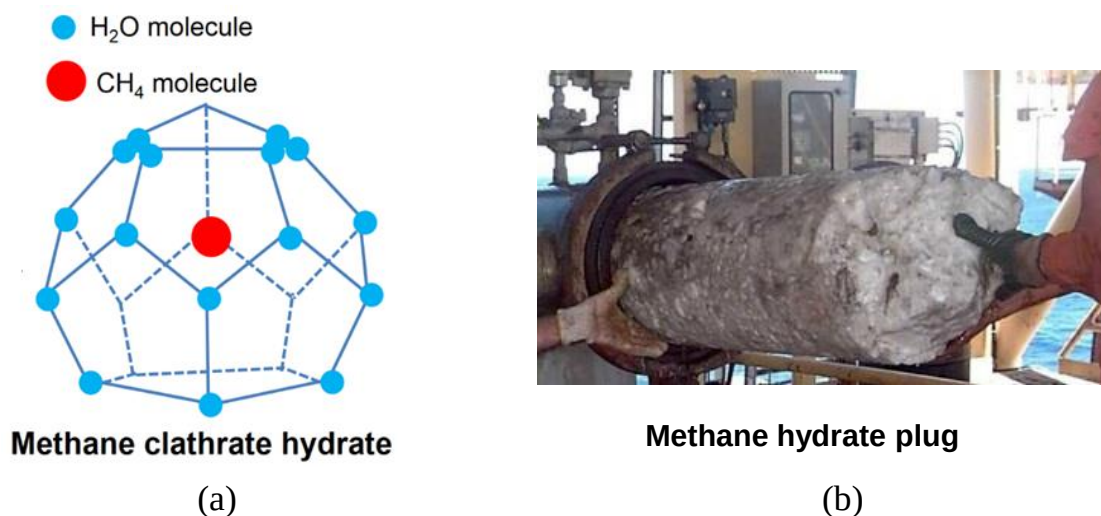


Figure 1.2. a) Structure of methane hydrate. b) Methane hydrate plug in a subsea pipeline [13].

creation, there are applications where promoting ice and hydrate nucleation is beneficial. For example, controlling nucleation has importance in cryobiology and food preservation science Figure 1.1(c) [16–18]. Additionally, controlling and promoting the nucleation of methane hydrates has important applications in methane harvesting, CO₂ sequestration, hydrogen storage, and desalination with hydrates [19–23]. In particular, hydrate-based natural gas storage is particularly appealing because at standard temperature and pressure, a cubic meter of natural gas hydrate yields 164 m³ of methane gas and 0.8 m³ of water, as shown in Figure 1.3.

In particular, the extraction of methane from methane hydrates as a natural energy source is garnering great interest. While estimates of the amount of methane in gas hydrates around the world vary, 20,000 trillion m³ is a commonly used estimate [25]. Figure 1.4 shows that hydrates hold the majority of organic carbon compared to other carbon sources. Based on these current estimates, 1% of the methane from the global methane hydrate reserves can meet the energy demands of the United States

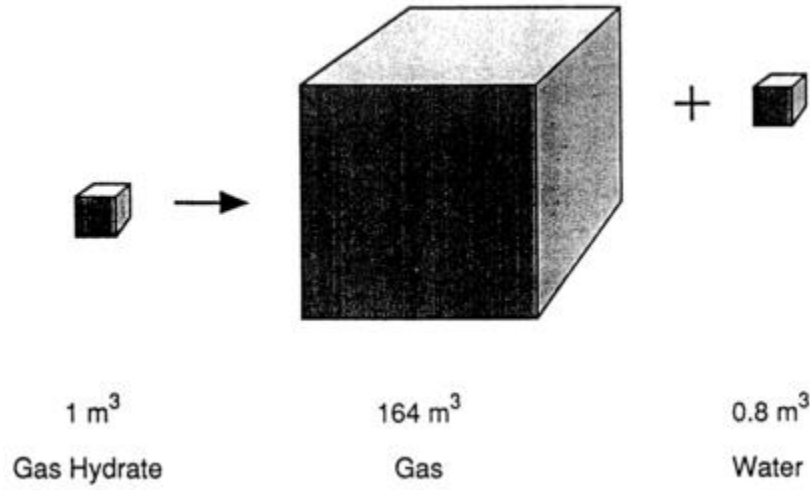


Figure 1.3. Gas hydrates can store an enormous volume of methane at standard temperature and pressure. Reprinted with permission from [24].

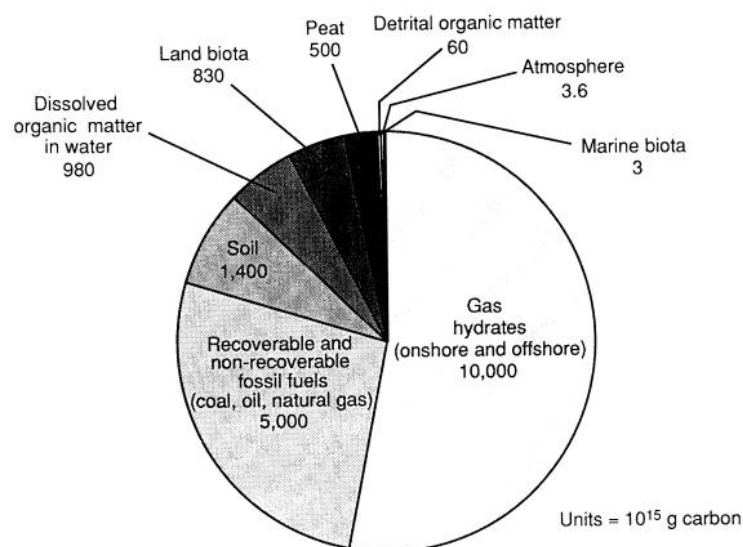
for the next eight decades [22].

1.1 Motivation for present work

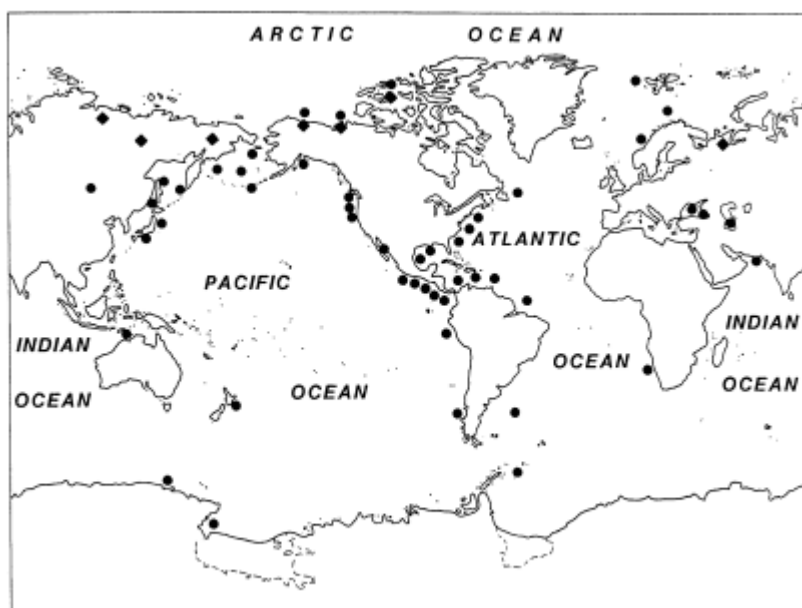
Despite the many and important applications related to controlling ice and hydrate nucleation, there are significant fundamental gaps in our understanding of ice and hydrate nucleation that must be addressed to enable new technologies in these fields. This dissertation includes three lines of enquiry that analyze various aspects of nucleation of ice and hydrates.

1.1.1 Effects of salt concentration in ice nucleation kinetics

Many studies [3–5, 26–39] have focused on analyzing and developing icephobic surfaces. It has clearly been observed that low surface energy translates to icephobicity, i.e., delayed ice nucleation and/or lower ice adhesion. However, an overwhelming



(a)



(b)

Figure 1.4. a) Distribution of organic carbon (excluding dispersed organic carbon, e.g., kerogen and bitumen) b) Worldwide locations of known and inferred gas hydrates in oceanic sediments (solid circle) and continental (permafrost) regions (solid diamond). Both images reprinted with permission from [24].

majority of studies on icephobicity have been about freshwater icephobicity. There are very few fundamental studies on ice formation kinetics with more complex fluids, such as saltwater. Saltwater or marine icing is vastly more complicated and highly understudied, despite its huge applications.

There are many different approaches used for deicing/anti-icing in marine applications, which include chemicals, coatings, special structure designs, heat, high-velocity fluids, and manual deicing [6]. However, these deicing/anti-icing technologies have been directly adapted from freshwater icing studies without an analysis of saltwater icing. In-depth studies that focus on the nucleation kinetics of saltwater do not exist.

1.1.2 Promoting ice nucleation with electric fields

The use of electric fields is a promising approach to promote and control the freezing of water. Electrofreezing has been shown to elevate the freezing temperature of water by applying an external electric field. This phenomenon was first reported in 1861 by Dufour [40]. In 1951, Rau [41] observed supercooled water droplets instantly freezing when an electric field was applied between two electrodes immersed within the droplets. In the 1960's and 1970's, Pruppacher [42–44] conducted experiments that demonstrated that freezing could be initiated by electrical discharges in the liquid. More detailed studies on electrofreezing have been performed in the last two decades. However, there are a significant number of unanswered questions related to the basic mechanism of electrofreezing and the influence of the electric field strength on the freezing temperature.

While most studies have shown that an applied electric field raises the freezing temperature, other studies [45, 46] have shown no effect. These disagreements result

from both the manner in which the electric field is applied and various secondary phenomena that can contribute towards nucleation. Additionally, it is likely that the polarity of the surface (for situations where nucleation is surface-dominated) plays an important role. Recently, Ehre et al. [47] demonstrated that negative surface charges lower the freezing temperature, whereas positive surface charges elevate the freezing temperature. Overall, there are important unanswered questions regarding the mechanism of electrofreezing (electric-field induced or current-flow induced) and the influence of the electric field magnitude on the freezing temperature elevation.

1.1.3 Inducing rapid formation of hydrates

Hydrates typically require long periods of time (on the order of days) before they start forming. This is problematic for many applications that require quick and controlled formation of hydrates (e.g., for desalination of water via hydrate formation). Currently, the two primary methods used to stimulate hydrate formation are mechanical agitation and chemical promoters, both of which increase the cost and complexity of hydrate production. There are no studies that have investigated the use of the electric fields to promote hydrate formation. Rapid hydrate formation in a quiescent system by the addition of stationary electrodes (to create an electric field) would enable many new hydrate-based technologies.

1.2 Literature Review

This section begins with a brief overview of homogeneous and heterogeneous freezing.

In homogeneous freezing, small ice nuclei continually form and melt within the fluid body. There is a competition between energy required to form a solid interface

and the lower energy state associated with a solid surface. Once a critical nucleus size is reached, further crystallization and solidification follows. However, homogenous freezing rarely occurs in the real world. Heterogeneous freezing occurs much more readily due to the presence of external nuclei, such as dust or dirt, which lower the required activation energy. The focus of this program of work is on heterogeneous freezing.

This section includes a literature review to identify gaps in knowledge associated with the three lines of study. The literature review is divided into three sub-sections. An overview of past work on icephobicity is presented in §1.2.1. §1.2.2 reviews past electrofreezing studies with a focus on identifying discrepancies and inconsistencies in past results. §1.2.3 is a review of past work on hydrate formation, which highlights the challenges associated with forming hydrates and reviews the current methods used to promote hydrate formation.

1.2.1 Past studies on freshwater and saltwater icephobicity

The development of anti-icing surfaces, i.e., icephobic surfaces, has been an active area of research for decades, as overviewed in [26, 27]. There are two primary strategies to achieve freshwater icephobicity. Firstly, the adhesion strength between ice and the surface can be lowered to enable easy ice removal from the surface. Most research efforts have focused on the premise that increased hydrophobicity lowers the adhesion between the surface and ice. The goal of the second strategy is to avoid ice accretion by preventing or delaying ice formation. Within this line of study, two types of experimental studies have been conducted. In the first type of studies, the impact dynamics of droplets on a superhydrophobic surface is analyzed to determine if water droplets can be repelled off the surface before they have time to freeze. In

the second type of experimental studies, the delayed freezing of static droplets on a superhydrophobic surface is characterized. Both types of experiments are idealized representations of real-world scenarios, i.e., droplets impacting a cold surface and droplets coming to rest on a cold surface followed by freezing.

There are numerous investigations into the relationship of surface wettability characteristics (e.g., static, receding, and advancing contact angles) and icephobic characteristics [28–30, 48]. Alizadeh et al. summarized the normalized ice adhesion strengths as a function of the water contact angle from a number of studies [48], as shown in Figure 1.5. The normalized ice adhesion strength is calculated as the ice adhesion strength on a coated surface divided by the adhesion surface on a bare surface. As can be seen in the figure, there is a general trend of lower adhesion as the contact angle increases.

While superhydrophobic surfaces can certainly decrease the energy required to detach ice from a surface, the second ice mitigation strategy aims to prevent or at least significantly delay ice formation and accretion. Many studies have investigated the delayed freezing of droplets resting on a variety of superhydrophobic surfaces [1, 2, 31–34]. However, much less attention has been given to how ice accretion begins when droplets impact cold surfaces.

A small number of studies have experimentally characterized the ability of superhydrophobic surfaces to repel impacting droplets before they freeze [35, 36, 38, 39]. Mishchenko et al. observed impacting droplets on various hydrophilic, hydrophobic, and superhydrophobic surfaces that were cooled to temperatures as low as -30°C , as shown in Figure 1.6 [35]. The authors found that ice formation could be completely prevented on superhydrophobic surfaces up to temperatures as low as -25 to -30°C . Alizadeh et al. highlighted the importance of droplet impact dynamics when

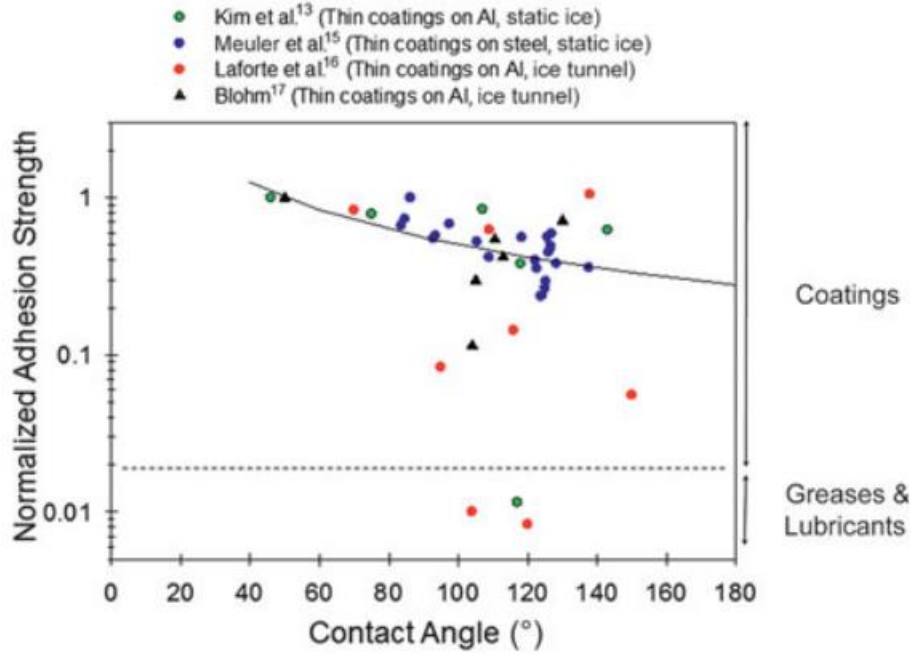


Figure 1.5. Normalized adhesion strength vs. contact angle for multiple icephobic surfaces. Reprinted with permission from [48].

investigating the icing kinetics of impacting droplets [39]. The authors found that the effectiveness of a superhydrophobic surface in delaying nucleation depends on the surface temperature.

As described above, research on icephobic surfaces to prevent or delay ice formation and/or ice accretion has been an active topic for many years. However, these studies have solely focused on *freshwater* icephobicity. Despite the large number of issues associated with icing in marine environments, saltwater icephobicity has largely been ignored. The rest of this subsection overviews the state of the art in the area of saltwater icing.

The freezing point depression of water by salt is well known [49], and a number of studies have investigated the extent of freezing point depression versus solute

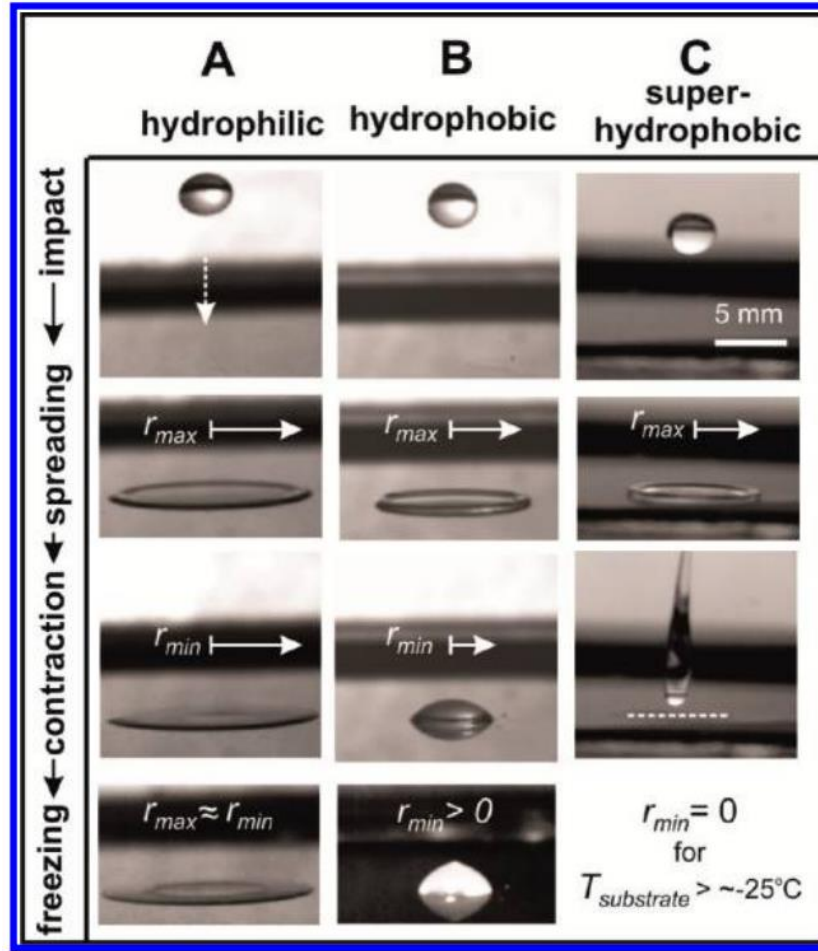


Figure 1.6. Images showing water droplets (15 μL) impacting a cold surface. The images show that pinning and ice formation occurred on the hydrophilic and hydrophobic surfaces, whereas complete droplet retraction was observed on the superhydrophobic surface. Reprinted with permission from [35].

concentration. Khvorostyanov and Curry developed analytical expressions for the freezing and melting critical temperatures for solutions with various chemical compositions, concentrations, and pressures, which agree well with reported data [50].

Early experimental work on saltwater freezing was conducted by Pruppacher, which showed that dissolved salt in water favors the formation of spongy and poly-

crystalline ice, and showed that the growth rate depends on the type of salt and salt concentration [51]. Recently, these results were experimentally and computationally verified by Bauerecker et al., who showed that the growth rate decreases with added salt due to requirement for salt ions to move over to the unfrozen brine (while the freezing front propagates [12]). Vrbka and Jungwirth carried out molecular dynamic (MD) simulations with atomic resolution to understand the molecular mechanisms underlying brine rejection [52]. This study indicates that the mechanism depends on the interplay between the moving salt ions and the freezing front progression; the salt density near the ice front reduces, followed by the formation of a new layer of ice. Carignano et al. also performed MD simulations on saltwater freezing and found that the freezing rate is affected by the pairing or clustering of ions [53]. Ayel et al. experimentally investigated the crystallization kinetics of water-MPG (monopropylene glycol) mixtures and showed that growth rate is an increasing function of the degree of supercooling and a decreasing function of the mass fraction of MPG [54]. Kimizuka and Suzuki experimentally investigated the nucleation temperature depression as a function of solute concentration and found that the self-diffusion coefficient of the solute is an important parameter [55]. However, all of the previous studies focused only on homogenous nucleation.

Zobrist et al. [56] and Wilson and Haymet [57] investigated heterogeneous nucleation and the effect of solute concentration. However, both studies focused on nucleation with ice nuclei; Zobrist et al. [56] used nonadecanol, silica, silver iodide, and Arizona test dust, while Wilson and Haymet [57] used sand grains as ice nuclei. There are no available studies that focus on the role of surface chemistry on ice nucleation with salt water.

A recent study by Boinovich et al., who also noted the lack of studies on

icephobic materials for saltwater, investigated the freeze time delays of static brine droplets on a superhydrophobic surface [58] and showed that there was a significant increase in the freezing delay time of brine droplets on a superhydrophobic surface compared with that of deionized water.

From the above summary, it is seen that systematic and focused studies on saltwater icephobicity are very rare. Clearly, more studies are needed to determine the influence of surface chemistry and morphology on saltwater freezing in a variety of environments. This is one of the central objectives of the present work.

1.2.2 Past studies on electrofreezing

Electrofreezing was first documented in 1861 by Dufour [40]; however, no details regarding the experiments or the mechanisms were provided. It was not until 1951 that the freezing of supercooled drops via electric fields was studied in more detail by Rau [41]. In his experiment, a highly polished chromium surface served as the negative electrode, upon which, millimeter-sized water droplets were placed. Two types of positive electrodes were used: a point electrode placed above the drop, and a spherical electrode covered with glass or amber that just touched the top of the drop. Rau found that freezing could only be instantaneously initiated by a spark between the droplet and the point electrode. Electric fields between 20-60 kV/cm were found to initiate freezing. Rau hypothesized that the electric field orients the water molecules in a way that promotes nucleation.

Pruppacher performed a series of electrofreezing experiments in the early 1960's and 1970's that began as a study on the phenomena occurring in clouds [42]. These studies were based on observations which suggested that a sudden rain pour was the result, not the cause, of lightning. Pruppacher first explored electrofreezing

using two metal electrodes that were submerged in paraffin oil to remove any possibility of sparks or corona discharge [42]. Water drops were either placed in oil or air between the electrodes. An electric field was applied when the supercooled droplets reached an equilibrium temperature. Pruppacher found that the application of the electric field at a certain threshold voltage could initiate nucleation; however, the study concluded that nucleation initiation was due to the movement of the droplet upon applying the electric field (fields of up to 30 kV/cm were used).

Currently, the most common experiment to demonstrate electrofreezing consists of bare metallic electrodes immersed in the fluid, as shown in Figure 1.7(a); an applied voltage sets up a volumetric electric field within the water. However, this also creates a small current flow in the liquid, which is demonstrated in the present work. It is therefore unclear if electrofreezing is the result of the electric field, or whether freezing is being promoted by the current flow and/or by the chemical reactions that occur at the water-electrode interface. Also, Joule heating is a complication that occurs during electrofreezing in this type of setup that has not been discussed in previous studies. Multiple studies [59–63] have clearly shown elevated freezing temperatures with applied voltage pulses using bare electrodes that pass current.

Very few studies have been conducted on electrofreezing in the absence of current flow, and even then, several unanswered questions remain. Wei et al. used two parallel plate electrodes with a water sample placed between the electrodes, though not in contact with either electrode [64]. With this configuration, they observed a supercooling temperature increase of 1.6 °C at electric field strengths of 1×10^5 V/m. However, the reported data are based on only three measurements and do not capture the stochastic nature of nucleation. A similar but statistically significant study with over one hundred measurements was conducted by Wilson et al. [45] and showed that

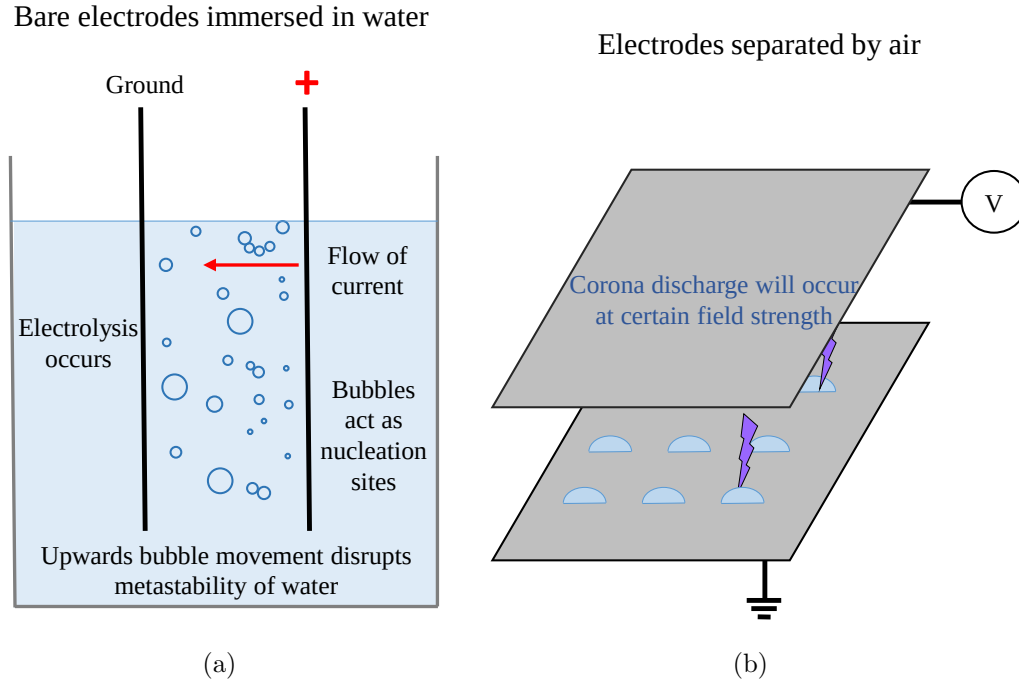


Figure 1.7. Commonly used experimental configuration for studies on electrofreezing. a) Bare electrodes immersed directly in water; b) Positive electrode located in air at a distance above droplets.

the freezing temperature was unaffected at electric field strengths up to 5×10^4 V/m. Similarly, Doolittle and Vali [46] found no difference in nucleation rates in electric fields as high as 6×10^5 V/m applied to droplets on a grounded plate, where a wire grid located above the droplets acted as the high-voltage, non-contact electrode (Figure 1.7(b)). More recently, Orłowska et al. [16] observed that electric fields approaching 1×10^6 V/m clearly accelerated nucleation in the absence of current flow; this electric field was one order of magnitude stronger than the previous efforts. It should be noted that the maximum applied electric field reported in electrofreezing is 6×10^6 V/m- a limitation imposed due to the occurrence of air ionization [16].

Overall, there are significant unanswered questions regarding the mechanism

of electrofreezing (electric-field induced or current-flow induced) and the influence of the electric field magnitude on the freezing temperature elevation. One objective of the present work is to isolate and quantify the influence of electric fields (surface charge) and electric current on ice nucleation in supercooled water droplets.

1.2.3 Past studies on hydrate formation and methods to promote hydrate formation

As mentioned in the introduction, hydrates consist of hydrogen-bonded water cavities that encage a guest molecule. Hydrates predominantly form into three types of structures (cubic structure I, cubic structure II, and hexagonal structure H), which depends on the guest molecule, as shown in Figure 1.8 [14]. Note that all common natural gas hydrates form one of these three structures [65]. When all of the cavities are filled, all three structure types have similar concentrations of approximately 85 mol.% of water and 15 mol.% of the guest material [14].

In 1810, Sir Humphrey Davy [65, 66] observed an ice-like solid that formed at temperatures above 0 °C; this was later revealed to be a chlorine hydrate. In 1823, Michael Faraday measured and reported the composition of chlorine hydrates; this was the first quantitative study of hydrates [65, 66]. In 1934, Hammerschmidt discovered that natural gas hydrates were blocking gas pipelines [67]. Subsequently, most of the interest in hydrate research stemmed from the oil and gas industry, with a focus on preventing methane hydrate formation in gas pipelines.

Early studies on hydrates investigated the thermodynamic conditions required for hydrate formation. This constituted a macro-perspective approach, where the end goal was to ensure that pipelines avoided such conditions [68–75]. More recent research has shifted focus to a more micro-perspective, with the objective of understanding the fundamental mechanisms underlying nucleation and growth of hydrates.

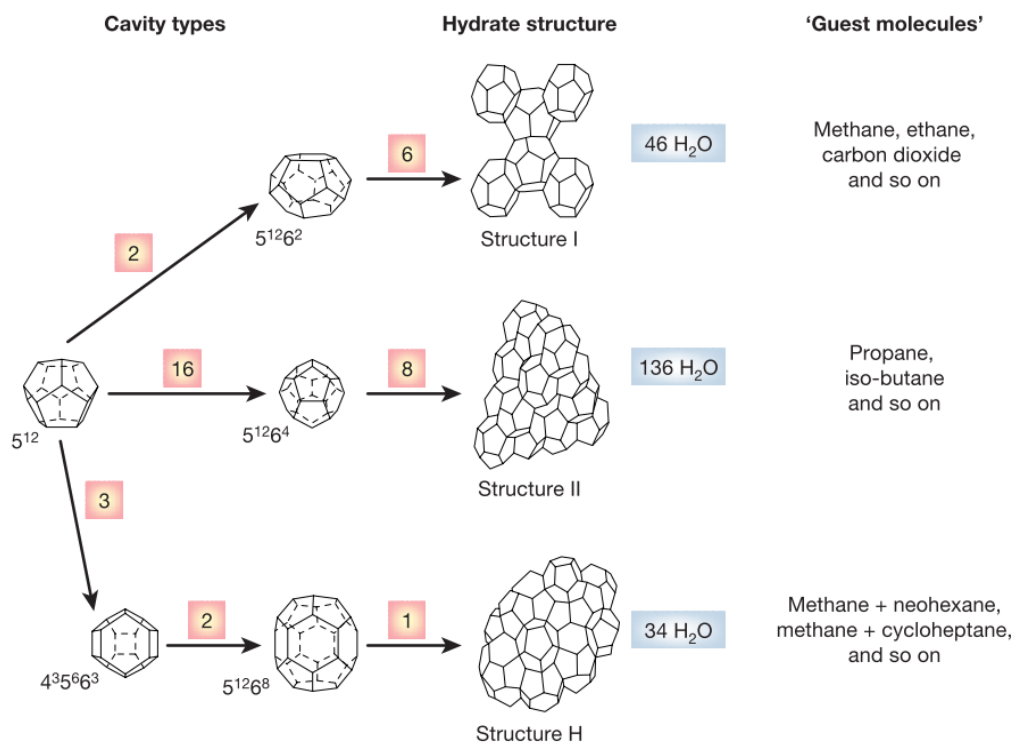


Figure 1.8. Illustration of the types of structures (structure I, II, and H) formed by common gas hydrates. Note that 5¹²6⁴ indicates a water cage composed of 12 pentagonal and four hexagonal faces. The numbers in the squares represent the number of cage types. Reprinted with permission from [14].

The application space for research on hydrates has also grown rapidly and now encompasses applications far beyond flow assurance [76–82].

Gas hydrates have generated significant interest because of their potential to store and transport natural gas. Other applications for hydrates includes CO₂ capture and sequestration, hydrogen storage, and flue gas separation. For all such technologies to become viable, three critical problems inherent to hydrate formation need to be overcome: long induction times, slow growth rates, and low water-to-hydrate conversion ratios.

Induction time is defined as the time interval required to form the very first hydrate ‘seed’ that is large enough for spontaneous further growth [83]. In experiments, induction time is the time period over which the temperature remains at the set value until a significant temperature change in the system is detected, which is due to the heat released upon hydrate nucleation [84]. Many hydrates, and in particular gas hydrates, suffer from excruciatingly long induction times.

As an illustration, methane hydrates require days to form [85, 86] in the absence of any active formation promotion methods. In fact, it is unusual to form a gas hydrate without the use of one of the hydrate formation promotion methods. Two methods that have been explored to reduce the long induction times are 1) mechanical mixing/agitation and 2) the addition of chemical promoters. Recently, the use of porous media to promote hydrate formation has also been investigated. All these approaches are discussed below. Table 1.1 compiles the induction times of methane hydrates from a number of studies, where different promotion techniques were investigated.

Vysniauskas and Bishnoi found that the consumption rate of methane gas during hydrate formation increased (which indicates accelerated hydrate formation) with the use of a magnetic stirrer. This was ascribed to the increased area of the gas-liquid interface [91]. The authors reported that a stirring rate greater than 400 rpm was required to remove the hydrate crystals formed on the liquid-gas interface and maintain a constant consumption rate; this hydrate layer at the interface was found to greatly affect the gas consumption. Englezos et al. also investigated methane hydrate formation and found that an increased stirring rate resulted in a shorter induction period [92]. Hussain et al. performed an extensive study on the effect of stirring rate on ethane hydrates and demonstrated that mixing controls both the rate and

Table 1.1. Compilation of induction times of methane hydrates using various promotion methods. It is noted that the experimental conditions (equipment used, pressure and temperature conditions, and water/methane composition) all affect the induction time. In the table, for each individual study, all of the aforementioned conditions remained the same. Thus, the effect the promotion technique can be qualitatively understood.

Authors	Year	Nucleation promotion technique	Induction time
Kamath and Holder [85]	1987	-	>24 hrs
E.D. Sloan Jr. [86]	1998	-	>24 hrs
Skovborg et al. [87]	1993	Stirring (200 rpm)	56 min
		Stirring (250 rpm)	19 min
		Stirring (300 rpm)	19 min
		Stirring (380 rpm)	12 min
Hao et al. [88]	2007	SDS	16 hrs
		Stirring + SDS	3.8 hrs
Ganji et al. [89]	2007	Stirring	>5 hrs
		Stirring + SDS (300 ppm)	<1 hr
		Stirring + SDS (500 ppm)	<30 min
		Stirring + SDS (1000 ppm)	1 hr
Ramaswamy and Sharma [90]	2011	-	>5 days
		SDS	3.8 hrs
		SDS + large bubble foam	3.6 hrs
		SDS + small bubble foam	2.5 hrs

extent of hydrate formation [93]. Other studies have also confirmed the positive effect of mechanical stirring on hydrate formation at various experimental conditions and for different hydrates [87, 88, 94, 95]. While mechanical stirring is the most popular method of agitation, other designs have also been proposed, such as using liquid spraying through a nozzle [96, 97].

However, in terms of practical usage in a large-scale hydrate formation facility, mechanical stirring/agitation increases the installation, operation, and maintenance costs of the system. Replacing mechanical agitation with a more passive technology (with no moving parts) will make many hydrate-based technologies more viable.

There are a number of studies that have investigated the use of chemical promoters, most notably, surfactants, to overcome the three primary challenges to hydrate formation. Numerous studies have focused on investigating the effect of surfactant type and surfactant concentration on the promotion of hydrate formation [84, 89, 98–104]. Many researchers have highlighted SDS (sodium dodecyl sulfate) as one of the best hydrate promoters [89, 99, 100, 104], which can increase the hydrate formation rates in a quiescent system by more than 700-fold [98]. Currently, researchers surmise that the mechanism underlying hydrate formation promotion by a surfactant can be explained on the basis of capillarity [104]. The addition of surfactants results in a morphological change in the hydrate, which ensures that gas-to-water contact is maintained. Instead of hydrate crystals forming a dense impervious film at the interface, thick, porous hydrate layers grow, which migrate towards the chamber walls; liquid is drawn via capillary forces to the crystallization front to maintain continuous gas/liquid contact [104, 105]. However, the use of surfactants can be expensive, requires monitoring, and involves environmental considerations. Any new method that eliminates the need for both moving parts and/or chemicals to form hydrates will be very appealing.

A relatively new method to promote hydrate formation is the use of porous media. Porous media is characterized by a high surface area to volume ratio, which makes it easier for gas molecules to contact water molecules [106, 107]. Furthermore, porous media in the form of metal foams can effectively transport the large amounts

of heat released during hydrate formation; this will increase the rate of hydrate formation.

The first studies on hydrate formation promotion using porous media investigated silica gel pores [106–108], glass beads [109–111], and silica sand particles [112]. Both Seo et al. and Adeyemo et al. showed that silica gel with small pore diameters (30–200 nm) could be used to remove CO₂ from flue gas (containing CO₂ and N₂). Both studies found that experimental setups with porous media had comparable performance with setups that used a stirred reactor or with excess water [106, 107]. Furthermore, Adeyemo et al. found that the crystallization rate and hydrate yield were considerably enhanced with silica gel and that this enhancement depended on the particle size [106]. Liu et al. found that porous media decreased the induction time of THF hydrate formation [111]; the porous media used was soda glass beads of different particles sizes (0.105–0.710 mm), where the porosities in all the tests were similar, approximately 0.35. The authors found that the average induction time decreased as the particle size was increased.

Additionally, the use of metal foam as the porous media has demonstrated great promise [113, 114]. Yang et al. experimentally investigated the effect of aluminum foam (average pore size of 1 mm) on the formation and growth kinetics of methane hydrates with 0.03 wt.% SDS but without stirring [113]. The results demonstrated that the aluminum foam not only accelerated the induction time but also increased the rate of formation (as much as 52%) and growth. The authors believed that the foam enhanced formation by increasing the number of methane-water contacts; furthermore, the foam’s large surface area and excellent thermal conductivity facilitated hydration heat removal.

Despite progress in promoting hydrate formation, state-of-the-art techniques

still require long induction times. Alternative approaches to enable rapid hydrate nucleation are therefore of great interest. Based on previous studies on electrofreezing, the role of electric fields is a promising avenue to reduce the induction time associated with hydrate formation. No prior work has investigated the influence of electric fields on hydrate nucleation. Only one related study by Kumano et al. has investigated the effect of an electric field on a tetra-n-butyl ammonium bromide (TBAB) aqueous solution [115], which forms a semi-clathrate hydrate [116]. The authors applied DC voltage through bare electrodes in a solution of TBAB and water, where the electrode material, supercooling temperature, and sample concentration were varied. The results showed that the probability of nucleation increased (100% nucleation under certain conditions) with the application of DC voltages. The nucleation probability was also found to depend on the electrode material, with the nucleation probability being particularly high for copper electrodes.

Clearly, additional studies are required to further investigate electrofreezing as a tool to achieve rapid hydrate nucleation. Combining electrofreezing with metal foams can potentially increase both hydrate growth rates and water-to-hydrate conversion ratios, thereby solving all three critical problems associated with hydrate formation. An important objective of the work in this dissertation is the development of the concept of electro-nucleation as a tool to induce rapid hydrate nucleation.

1.3 Objectives of research program

The strategic goal of the present research program was to enhance the fundamental understanding of ice and hydrate nucleation and develop concepts to promote or hinder nucleation using passive and active means. Passive methods investigated in this program of work include the use of surface chemistry and surface texture to

control nucleation. The active method studied in this work is the application of an electric field to promote nucleation. More specifically, the research program is organized around three objectives. These objectives and the pathway employed in these studies are briefly summarized ahead.

Objective 1: Compare saltwater and freshwater ice nucleation

Statistically meaningful studies of heterogeneous ice nucleation were conducted to understand the role of surface chemistry, surface texture, and salt concentration on saltwater ice nucleation. A custom-built environmental chamber was developed for these experiments. A liquid nitrogen-controlled cold plate was used to lower the surface temperature. Infrared imaging and high-speed visualization was employed to track the thermal signatures and impact kinetics of droplets, respectively.

Two kinds of experiments were conducted. In the first set of experiments, the freezing temperatures of static water droplets (freshwater and saltwater) were measured on surfaces with contrasting chemistries. In the second set of experiments, the benefits of superhydrophobic surfaces in preventing icing during impact of saltwater droplets were studied.

Fundamental questions answered by the studies related to Objective 1

- *How is saltwater ice nucleation different from freshwater ice nucleation?*
- *What is the influence of surface chemistry on the freezing temperatures of saltwater droplets?*
- *Does the presence of salt in water change the impact dynamics of water droplets on supercooled substrates?*

- *Are superhydrophobic surfaces better at preventing saltwater icing as compared to freshwater icing?*

Objective 2: Study the role of electric fields on the nucleation of super-cooled water droplets

There are very conflicting conclusions from existing studies on the role of an electric field in elevating the freezing temperature, a phenomenon referred to as electrofreezing. Some studies have shown that an electric field can promote freezing, and other studies have concluded that there is no such effect. Several studies have suggested that secondary effects, such as chemical reactions on the electrodes, are responsible for elevating the freezing temperature.

To isolate the effect of electric field (resulting in an interfacial surface charge) from electric currents, an experimental setup was designed, which prevented current flow through the liquid solution of interest. This was accomplished by placing a dielectric layer between an immersed wire electrode in the fluid and a metal wafer electrode underneath the dielectric layer. In this configuration, the electric field concentrates at the solid-liquid interface (instead of a volumetric electric field in the liquid), and the dielectric layer prevents current flow.

With the use of the dielectric layer, electric fields that are an order of magnitude greater than any applied field reported in literature can be applied. The temperature-time histories of water droplets were measured using an infrared camera. The onset of nucleation was detected via a temperature spike. The average freezing temperature at different electric fields and polarities was obtained for a large number of droplets. Furthermore, by intentionally creating pinholes in the dielectric layer to induce current flow, the effect of electrolysis/bubble formation/chemical reactions was isolated. Bubble formation and electrolysis were visually observed via

high-magnification, high-speed visualization, and current flow was measured with an ammeter in the electrofreezing circuit.

The results of these experiments reveal that while electrofreezing can be explained by the presence of an electric field (and interfacial charge) only, secondary effects associated with current flow can further elevate freezing temperatures.

Fundamental questions answered by the studies related to Objective 2

- *What is the basic mechanism underlying electrofreezing, i.e., is it electric field-induced or electric current-induced?* Past studies have shown an elevation in freezing temperature when an electric field is applied; however, the results have always been confounded by the presence of simultaneous secondary phenomena.
- *Is there a limit to electrofreezing-induced freezing temperature elevation?* This study shows that the electrofreezing effect saturates at higher electric fields. Electric field strengths that are an order of magnitude greater than those reported in literature were used in the present work.
- *What is the effect of surface polarity on electrofreezing?* There has only been a single study that has investigated the effect of polarity in electrofreezing [47].
- *How does current flow/electrolysis/bubble formation affect electrofreezing?* The effects of electric fields and current flow have not been investigated separately. By isolating the role of electric fields and then subsequently allowing current flow to occur, the relative importance of each effect can be isolated.

Objective 3: Study and develop the concept of ‘electro-nucleation’ as a tool to induce rapid formation of hydrates

The results from the work related to Objective 2 strongly suggests the utilization of electrofreezing to promote the nucleation of hydrates. It is a well-known fact that hydrate formation involves very large induction times; it is expected that ‘electro-nucleation’ can reduce these induction times substantially. There are no existing studies that investigate the role of electric fields and current on the nucleation kinetics of hydrates. Proof-of-concept experiments were devised to measure the induction times of tetrahydrofuran (THF) hydrates in constant-temperature experiments. THF hydrates can form at atmospheric pressure, which makes these hydrates amenable for lab studies. In fact, THF hydrates are commonly used as a model hydrate in place of methane hydrates, which require high temperature and high pressure experimentation.

Mixtures of THF and water were cooled to a constant temperature below the formation temperature of THF hydrates. Electrodes were immersed in the solution to setup an electric field and electric current flow. The effects of increasing the voltage and current on the induction times associated with THF hydrate formation were measured. It was observed that rapid nucleation (< 10 minutes) can be achieved at a voltage of 100 V. This is a disruptive advancement in the field of hydrates since best-in-class techniques still involve moving parts and/or additives.

The results of this study suggests that electro-nucleation can be adapted to enhance promotion of gas hydrates; this advancement can enable many new hydrate-based applications, which have not been possible due to the slow rates of hydrate formation.

Fundamental questions answered by the studies related to Objective 3

- *Does ‘electro-nucleation’ of hydrates work?*

- *What is the role of an electric field and current on hydrate nucleation promotion?*
- *What is the entitlement of ‘electro-nucleation’ on nucleation promotion? Is it possible to achieve instantaneous hydrate nucleation using electric fields?*

1.4 Organization of rest of dissertation

This dissertation is organized into five chapters. Following this introduction and literature review (Chapter 1), Chapters 2-4 present the studies related to the above three objectives with one chapter for each objective. Each chapter contains descriptions of the experimental setup, methods, analysis techniques, and discussion of the results. Chapter 5 highlights the conclusions and advancements from the present work and details suggestions for future work. Appendix A describes the analysis to estimate surface temperatures reported in Chapters 2 and 3. Appendix B presents raw data corresponding to a set of experiments in Chapter 4. Appendix C describes a high-pressure cell that was reconfigured to synthesize methane hydrates and will be used in future studies. Appendix D includes the abstract of a journal publication that was based on my Ph.D. dissertation work under my former advisor, Prof. Alexandre K. da Silva.

Chapter 2

Influence of surface chemistry and texture on saltwater icing¹

This chapter details experimental studies to understand the influence of surfaces (chemistry, texture) on saltwater ice nucleation (Objective 1). Two types of experiments were conducted with saltwater: (1) freezing of static droplets and (2) freezing of droplets upon impact on a supercooled surface. The experiments with static droplets isolate the influence of surface chemistry on saltwater ice nucleation. The droplet impact experiments evaluate the utility of superhydrophobic surfaces for saltwater icephobicity through a study of saltwater droplet impact dynamics. Noting the lack of studies on saltwater freezing in literature, the work presented in this chapter is an important bridge between the widely studied freshwater icephobic surfaces and saltwater-related applications.

2.1 Experimental methods and procedures

Figure 2.1 shows a schematic of the experimental setups. All experiments were conducted in a custom-built, air-tight acrylic environmental chamber. The chamber (inside dimensions of 0.43 m x 0.45 m x 0.3 m) was made from acrylic and housed a liquid nitrogen-cooled cold plate (Instec, HCP306SC). The cooling area was 0.15 m x 0.15 m. An infrared (IR) camera (FLIR, A655sc) was used to measure the

¹Material from this chapter has been published: Carpenter, K., and Bahadur, V., 2015. "Saltwater icephobicity: Influence of surface chemistry on saltwater icing". *Scientific Reports*, **5**, p.17563.

temperature-time history of the droplets and detect the onset of nucleation, as explained later in this chapter. It should be noted that this technique has been previously used by multiple researchers to detect the onset of freezing [12, 34, 37]. The IR camera had an accuracy of $\pm 2^\circ\text{C}$ or $\pm 2\%$ of the reading. The spectral range, resolution, detector pitch, and NEDT of the camera are 7.5-14 μm , 640×480 , 17 μm , and <50 mK, respectively. A 5.8x lens (FLIR, T198060) was used for magnification. An IR-transparent germanium window (ISP optics) was installed at the top of the chamber. The germanium window has an average transmittance greater than 0.96 in the 7-13 μm wavelength range. To reduce the humidity, the chamber was flushed with nitrogen gas before beginning the experiments. A hygrometer (Fischer Scientific, 11-661-18) was used to monitor the chamber humidity. A high-speed camera (Photron Mini-UX-100) was also used to observe freezing. This camera has a pixel resolution of 1280×1024 at 4000 frames per second. The lens used was a Model K1 CentriMax from Infinity. The high-speed camera was placed behind one of the side walls of the environmental chamber, where a glass window was installed.

Three fluids were used for all the experiments in this chapter: deionized (DI) water (henceforth referred to as pure water), a 0.6 M NaCl solution (which represents the average salinity of the ocean and henceforth referred to as seawater), and a 3 M NaCl solution (henceforth referred to as brine). The sodium chloride to make the salt solutions was purchased from Sigma Aldrich ($>99.5\%$ purity).

2.1.1 Experiments on ice nucleation in static saltwater droplets

These experiments measured the ice nucleation temperature and the freezing propagation kinetics of static droplets of three fluids on two different surfaces. To investigate the role of surface chemistry on nucleation kinetics, two surfaces with con-

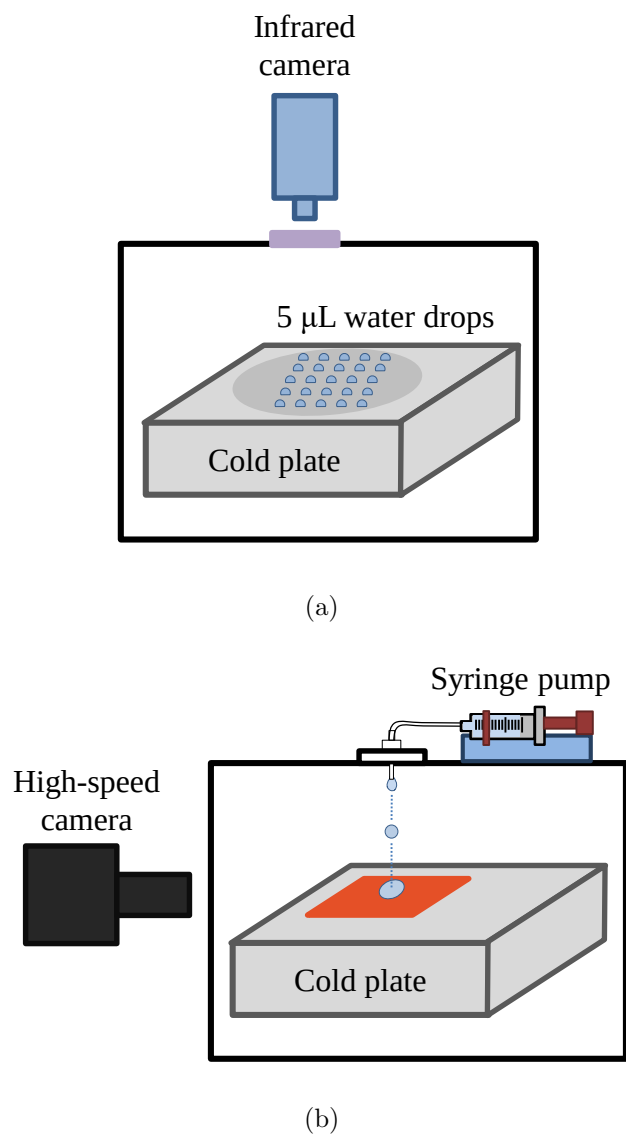


Figure 2.1. Schematic of the experimental setups for a) studying nucleation of static saltwater droplets and b) saltwater droplet impact on supercooled superhydrophobic surfaces.

trasting surface chemistries were used: hydrophilic aluminum surfaces (high surface energy of 169 mJ/m^2 [117]) and hydrophobic Teflon-coated surfaces (low surface energy of 19 mJ/m^2 [117]). The aluminum surface was a polished wafer with a diameter of 100 mm and thickness of 0.8 mm. To fabricate a Teflon surface, Teflon (DuPont, AF1600) was spincoated onto the aluminum wafer at 1000 rpm. The sample was then cured on a hot plate at 240°C for approximately 10 minutes.

Figure 2.2 describes the methodology to detect ice nucleation by tracking the temperature of a droplet by an IR camera [37]. The onset of nucleation is accompanied by a sudden temperature spike due to the latent heat release. The temperature stays uniform while the freeze front propagates and the entire droplet freezes; after which, the frozen droplet cools to the substrate temperature. It should be noted that the IR camera measures the temperature at the top of the droplet, which is close to 0°C during freezing, as reported in another experimental study [37]. This measurement was then used in a 1-D thermal model to estimate the solid-liquid interface temperature at which freezing occurred (see Appendix A).

In the FLIR software, a one-pixel point in the middle of the droplet was chosen to represent the droplet temperature. The software recorded the droplet temperature versus time of each droplet in every experiment. A MATLAB code was written to determine the freezing temperature of each droplet from the data file created in the FLIR software.

The experiments involved two hundred droplets for a particular surface-fluid combination. It should be noted that such statistically relevant data sets are not reported in most nucleation studies. Furthermore, great care was exercised to ensure that salt contamination did not affect the measurements. To reduce the possibility of contamination, the surface was cleaned after each experiment (acetone, isopropanol,

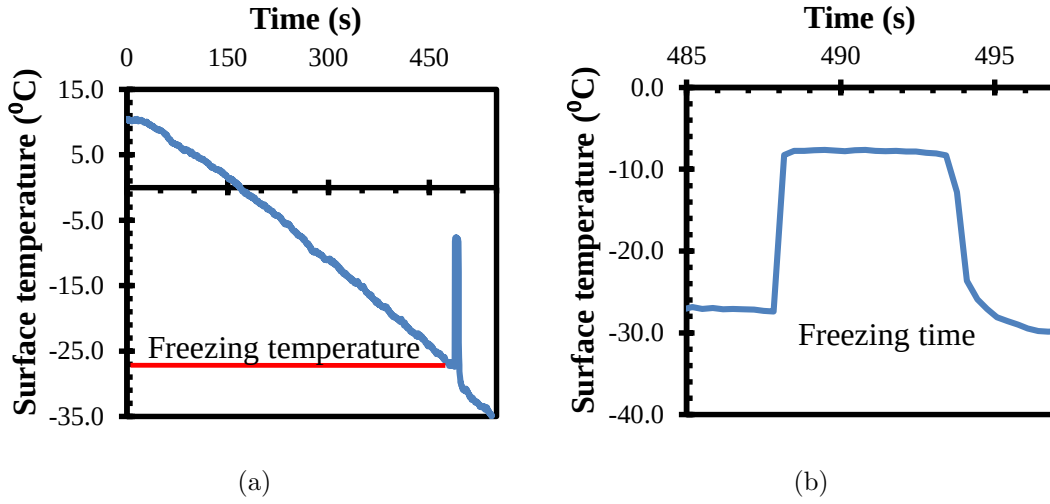


Figure 2.2. a) Illustrative temperature-time curve showing the onset of freezing and b) details of the temperature spike following the initiation of nucleation (due to release of latent heat), followed by a constant temperature until the entire droplet freezes.

DI water) and then dried on a hot plate. Also, because the experiments are targeted at isolating the influence of surface chemistry on nucleation, the entire setup was mounted on a vibration-free table. Common external triggers for nucleation, such as shocks and air drafts, were substantially eliminated in this setup.

This setup was used to measure the freezing temperature and freeze front propagation kinetics in 5- μ L droplets. Initially, the plate temperature was set at 15 °C, and 50 droplets were manually deposited on the surface. The chamber was then closed and flushed with nitrogen to remove moisture. When the relative humidity reached less than 1%, the infrared (IR) camera was turned on, and the plate was set to cool at 5 °C/min. The experiment ended when all droplets had frozen, which could be visually observed when the droplets changed from clear to opaque.

2.1.2 Experiments on impact dynamics of saltwater droplets

The objective of the second set of experiments was to gain an understanding of the influence of superhydrophobic surfaces on saltwater ice mitigation. The primary avenues to reduce ice buildup include nucleation delay and reduced ice adhesion. It is expected that the benefits of superhydrophobic surfaces will be amplified by the intrinsic freezing point depression of saltwater. The impact icephobicity of a superhydrophobic surface can be characterized by the ability of the surface to repel water at low temperatures [35]. Mishchenko et al. [35] estimated the ice prevention ability of superhydrophobic surfaces by studying single droplet impact dynamics to estimate the lowest temperature at which droplets are repelled. Multiple studies [35, 118] have discovered that superhydrophobic surfaces repel pure water at temperatures as low as -20°C to -30°C ; it is expected that saltwater will be repelled at even lower temperatures. This hypothesis was the basis of the present impact experiments, in which the ability of a superhydrophobic surface to repel saltwater at low temperatures was investigated.

The droplet impact experiments (Figure 2.1(b)) were conducted in the same environmental chamber as the static tests. 2.2-mm diameter droplets of the three liquids (pure water, seawater, and brine) were released from a syringe pump from a height of 20 cm, which corresponds to an impact velocity of 2 m/s on the cold plate. All of the droplets were initially at room temperature. Droplet impact dynamics were recorded using a high-speed camera at 4000 fps. Before each test, the chamber was flushed with nitrogen, and the plate was cooled to the desired temperature. Five minutes later, a droplet was released to impact the surface, and the droplet-surface interaction was recorded by the high-speed camera. After each impact experiment, the surface was moved, and the next impact experiment was conducted without opening

the chamber. This procedure was repeated for all three liquids, and at least five droplet impact experiments were conducted per surface per temperature for each liquid. Note that the surface temperature was essentially the same as the plate temperature, which was determined by the experiments and analysis described in Appendix A.

2.1.3 Fabrication details

The superhydrophobic surfaces used in the droplet impact experiments were made on copper plates purchased from McMaster (99.9% purity). Multiple samples (10.1 cm long, 3.8 cm wide, and 3.15 mm thick) were made. The top surface of each sample was roughened using 80 grit sandpaper followed by 220 grit sandpaper. The samples were then cleaned with soap water and rinsed with deionized water followed by sonication in acetone for 10 minutes to remove any particles in the crevices. The samples were then dried on a hot plate at 115 °C for 10 minutes. Teflon AF1600 was then spincoated at 2750 rpm for 30 seconds followed by curing on a hotplate at 260 °C for approximately 25 minutes. The Teflon layer was approximately 1 μm thick.

The surface roughness of the superhydrophobic surfaces was measured by a profilometer (Detak 6M Stylus). The roughness was measured at three different positions on each Teflon-coated surface. Table 2.1 presents the average surface roughness from three measurements for each sample and the standard deviation.

The static contact angle and the standard deviation of a pure water droplet on this surface was 131° and 1.3°, respectively, which is based on eight contact angle measurements on four of the tested surfaces (two measurements on each surface). At room temperature, a 2.2-mm diameter pure water droplet could bounce approximately 4-6 mm off this surface.

Table 2.1. Surface roughness of superhydrophobic surfaces used in the droplet impact experiments.

Sample	Surface Roughness (nm)	
	Average	Std. Dev.
-10 °C	1036	118
-20 °C	1040	164
-20 °C	925	122
-30 °C	1460	104
-30 °C	987	102
-30 °C	1059	19
-30 °C	939	152
-40 °C	942	253
-50 °C	1005	127

It should be noted that great care was taken to avoid surface contamination (due to salt) in these experiments. In particular, each impact experiment was conducted on a different portion of the substrate; numerous samples were fabricated due to the large number of experiments. These surfaces had consistent surface chemistry and structure, which was verified by the surface roughness and contact angle measurements.

2.2 Results

2.2.1 Experiments on nucleation in static droplets

Several studies have characterized freezing kinetics in terms of the induction time [5, 33, 118]. Alternatively, other studies have characterized freezing kinetics in terms of the freezing temperature as the surface is cooled down [1, 31, 119–121]. While both the induction time and freezing temperature can be used to characterize the

influence of a surface on nucleation, this study uses the latter approach.

Figure 2.3 shows the average measured freezing temperatures for pure water, seawater, and brine droplets on aluminum and Teflon surfaces. Each bar in Figure 2.3 is the average of two hundred measurements over four sets of experiments involving fifty droplets each. It should be noted that the temperatures in Figure 2.3 are the surface-water interface temperatures, which are calculated based on the plate temperature and the temperature at the top of the droplet, as described in Appendix A. The error bars were calculated using the t-value and a 95% confidence interval, defined as the following equation:

$$95\% \text{ Confidence interval} = \pm t_{95,\nu} \cdot \frac{s}{\sqrt{N}} \quad (2.1)$$

where $t_{95,\nu}$ is the t-value for the 95% confidence interval, N is the number of samples, s is the standard deviation of the N samples, and ν is the degrees of freedom, which is $N-1$.

Figure 2.3 shows the freezing point depression as the salt concentration increases. It is seen that brine droplets freeze at least 15 °C lower than pure water and were observed to remain liquid at temperatures approaching -45 °C. Interestingly, and unexpectedly, surface chemistry does not have a measureable influence on the heterogeneous freezing temperatures of pure water and seawater, i.e., the average freezing temperatures were similar on both the Teflon and aluminum surfaces. However, there is a noticeable difference in the freezing temperature of brine droplets on the Teflon surface compared to the aluminum surfaces with a lower freezing temperature on the Teflon surface.

These experiments provide insights into the mechanisms involved in heterogeneous freezing of saltwater solutions. Firstly, it was verified via high-speed imaging

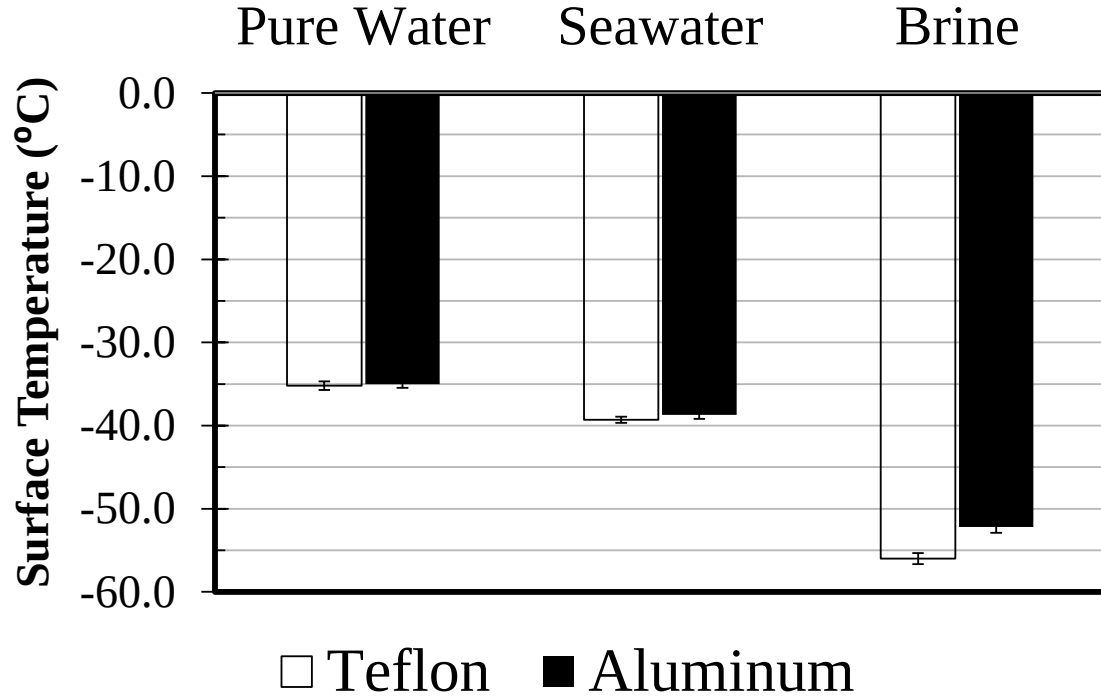


Figure 2.3. Average freezing temperature of pure water, seawater, and brine droplets on Teflon and aluminum surfaces (cooling rate of 5 °C/min). Each bar represents the average of 200 freezing experiments.

that nucleation originated at the three-phase contact line for pure water and saltwater. These results imply that surface chemistry on its own does not affect nucleation initiation; the differences in the freezing temperatures can be attributed to the thermodynamic freezing point depression with salt addition. There is a 3 °C difference in the nucleation temperatures of brine droplets on Teflon and aluminum. While the reasons for this difference are not clear, one possible explanation is frost formation near the droplet, which is difficult to prevent at such low temperatures. Frost formation rates were observed to be higher on aluminum than Teflon, and frost formation could have triggered ice formation in droplets on the aluminum surface at higher temperatures.

Overall, the present statistically relevant experiments show that surface chemistry on its own does not substantially alter the freezing temperature of static saltwater and pure water droplets. This also implies that any enhanced icephobicity benefits of superhydrophobic surfaces with saltwater can be attributed to surface roughness effects and the difference in impact characteristics of pure water and saltwater droplets.

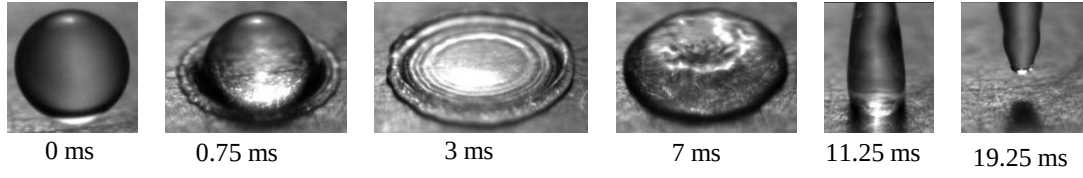
2.2.2 Saltwater droplet impact dynamics

Droplet impact dynamics were experimentally studied to estimate the differences in saltwater versus pure water dynamics and judge the utility of superhydrophobic surfaces in preventing saltwater ice.

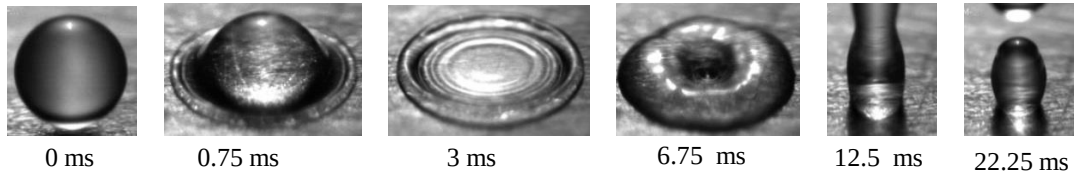
Figure 2.4 shows images of pure water droplets impacting the superhydrophobic surface at surface temperatures of $-10\text{ }^{\circ}\text{C}$, $-20\text{ }^{\circ}\text{C}$, $-30\text{ }^{\circ}\text{C}$, and $-40\text{ }^{\circ}\text{C}$. In all of these experiments, the spreading stage lasted for 2-3 ms, where the droplet spread to approximately 6 mm. The retraction profiles, however, varied significantly, and the extent of retraction was seen to depend on the surface temperature. At $-10\text{ }^{\circ}\text{C}$, the water droplet retracted completely under the action of surface tension and bounced off the surface. At $-20\text{ }^{\circ}\text{C}$, the droplet did not completely retract, and the entire droplet volume was not repelled from the surface. At $-30\text{ }^{\circ}\text{C}$, droplet retraction was further subdued. This behavior has been documented by other researchers [3, 35], who report the transition temperature at which a droplet fails to bounce off a superhydrophobic surface as between $-20\text{ }^{\circ}\text{C}$ to $-30\text{ }^{\circ}\text{C}$, which matches the present observations. A drastic change was seen at $-40\text{ }^{\circ}\text{C}$, wherein water droplets did not retract at all and remained pinned in the maximum spreading position.

Image processing can provide quantitative data for use in analyses and comparisons. Figure 2.5 shows the time-dependent droplet diameter during spreading and

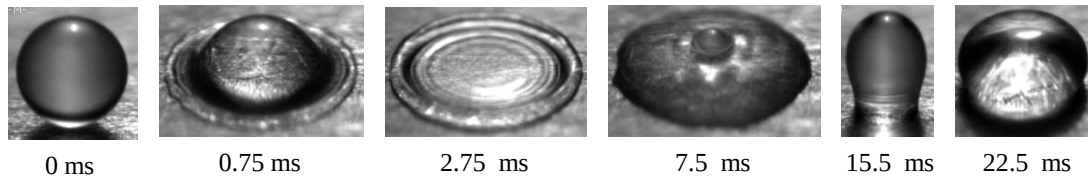
Surface temperature = -10 °C: Full retraction and full repulsion



Surface temperature = -20 °C: Partial retraction and partial repulsion



Surface temperature = -30 °C: Partial retraction and no repulsion



Surface temperature = -40 °C: No retraction and no repulsion

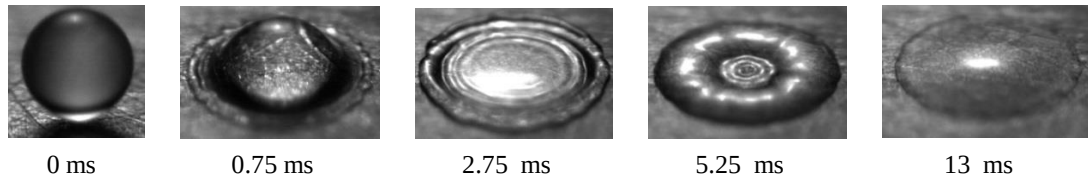


Figure 2.4. Contact line retraction and repulsion of pure water droplets (2.2 mm initial diameter) on a superhydrophobic surface at -10 °C, -20 °C, -30 °C, and -40 °C.

retraction at various surface temperatures with pure water droplets. The spreading phase is the same and independent of surface temperatures. However, the retraction profiles are markedly different, as depicted in Figure 2.5. In general, lower temperatures make retraction more sluggish, which matches the observations of Alizadeh et

al. [37].

An important objective of this work was a comparison of saltwater droplet impact dynamics at various surface temperatures. Figure 2.6(a) shows the impact dynamics of the three liquids at $-10\text{ }^{\circ}\text{C}$. It was seen that all three liquids showed identical profiles during the spreading stage. The retraction profiles varied slightly, but all three droplets had enough energy to completely come off the surface. Figure 2.6(b) shows the impact dynamics at $-30\text{ }^{\circ}\text{C}$ for the three liquids. It is seen that the retraction profiles are noticeably different with the brine droplet retracting more than the other two droplets. While none of the droplets completely left the surface, the brine and saltwater droplets recoiled significantly more than pure water droplets. Figure 2.6(c) compares the impact behavior at $-40\text{ }^{\circ}\text{C}$ for the three types of fluids. Both pure water and seawater showed poor retraction, but the brine droplet was

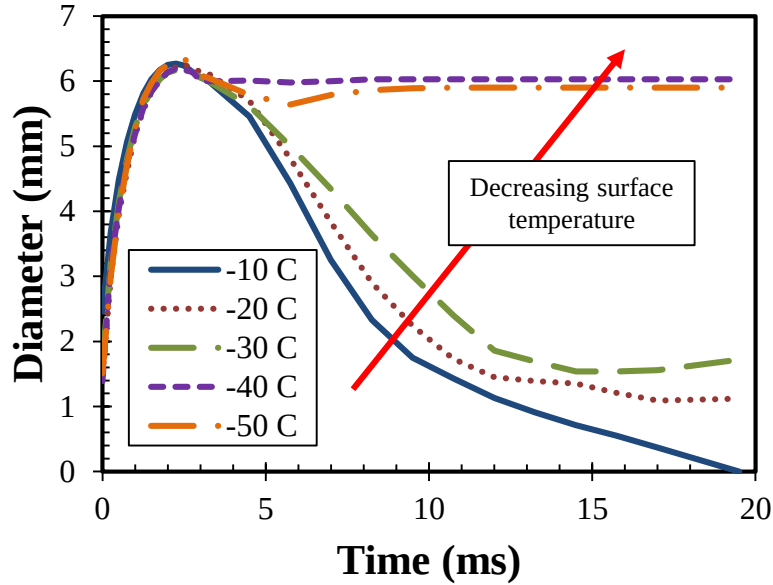


Figure 2.5. Time-dependent position of the contact line for pure water droplet impact at different surface temperatures.

able to retract about halfway. Figure 2.7 shows the differences in the retraction profiles of the three types of fluids at various surface temperatures. For all fluid types, the droplet impact behaviors are the same at the highest and lowest surface temperatures, i.e., complete repulsion at -10 °C and hardly any retraction at -40 °C; however, different temperature-dependent impact behaviors emerge at intermediate surface temperatures.

Based on analyses of droplet impact patterns, I propose two parameters to characterize the effectiveness of a surface in reducing ice buildup upon liquid impact. The first parameter is the retraction ratio after droplet impact, with the final retraction position normalized by the maximum spreading diameter. A value of 1 corresponds to complete expulsion of the droplet from the surface, which implies icephobicity under liquid impact conditions. However, this parameter on its own cannot completely quantify the anti-icing performance of a surface. In many experiments, it was observed that the droplet does not retract completely, but significant volumes of the droplet pinch out from the pool of liquid stuck to the surface.

The second parameter to judge the effectiveness of a superhydrophobic surface is the fraction of the liquid repelled after impact. This parameter was measured by estimating the volume of liquid left behind on the surface via image processing. A value of 1 implies that no fraction of the droplet is left behind, which translates to complete icephobicity upon liquid impact. It is important to note that conclusions about the effectiveness of superhydrophobic surfaces in repelling water are made by jointly considering both these parameters and not by considering a single parameter alone. It should also be noted that a retraction ratio of 1 implies that the fraction of the liquid repelled is also 1 by definition. However, the reverse is not true in cases where liquid is ejected off a droplet that has stopped retracting.

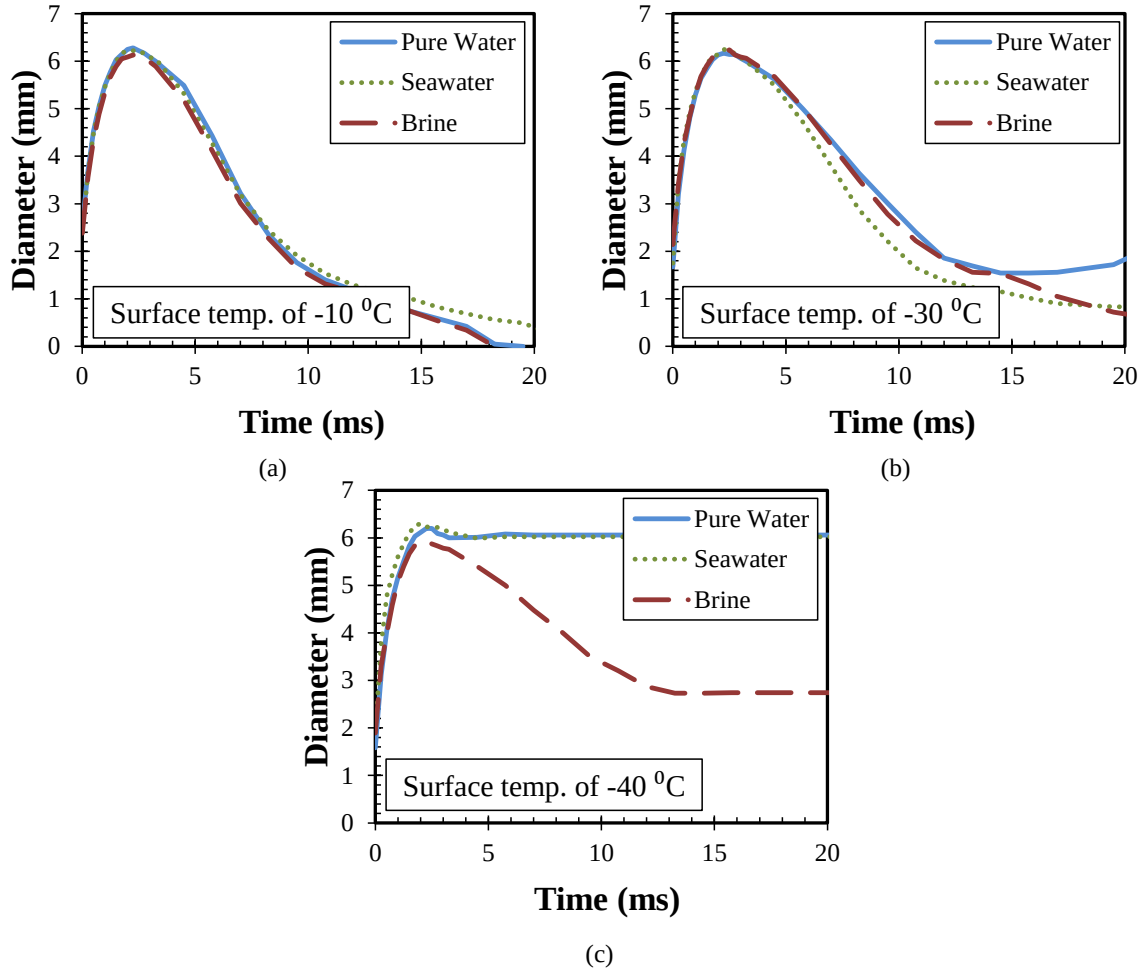


Figure 2.6. Time-dependent droplet diameter for the three liquids at surface temperatures of a) -10°C , where all droplets are repelled, b) -30°C , where no droplet is completely repelled, but the retraction characteristics are markedly different, and c) -40°C , where only brine droplets show measurable retraction.

Figure 2.8 and Figure 2.9 show the two parameters (retraction ratio and fraction of liquid repelled) for the three liquids at various surface temperatures. It should be noted that these results are the average of at least five experiments; the error bars are calculated using the t-value and a 95% confidence interval (Eqn. 2.1). As can be clearly observed from the two plots, all three fluids transition from complete

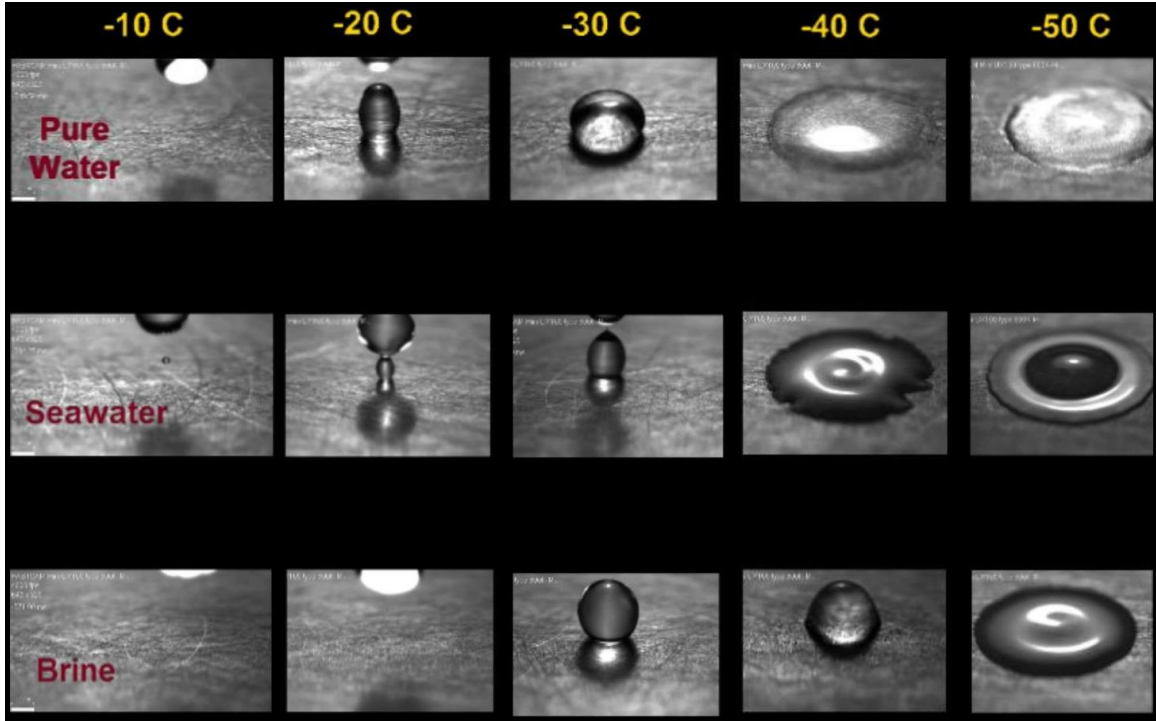


Figure 2.7. Images showing the final state of droplets after impact and retraction at various surface temperatures. At $-10\text{ }^{\circ}\text{C}$, all three fluids were completely repelled off the surface. At $-50\text{ }^{\circ}\text{C}$, all three fluids did not demonstrate any retraction. Within the temperature range of $-10\text{ }^{\circ}\text{C}$ to $-50\text{ }^{\circ}\text{C}$, the outcome of droplet impact was seen to be dependent on the composition of the droplet and the surface temperature.

retraction and bouncing off the surface at $-10\text{ }^{\circ}\text{C}$ to no retraction (Figure 2.8) and no liquid repelled at $-50\text{ }^{\circ}\text{C}$ (Figure 2.9). We define the transition temperature range as one over which the retraction ratio changes significantly. Importantly, this transition temperature depends on the salt concentration when other parameters are held constant. At $-20\text{ }^{\circ}\text{C}$, all three solutions show very high droplet retraction (Figure 2.8); however, the pure water and the seawater droplets have substantial liquid left on the surface, whereas the brine droplet is completely repelled (Figure 2.9). At $-30\text{ }^{\circ}\text{C}$, much more liquid repulsion is observed for the brine droplets (Figure 2.9); this

corresponds to the higher retraction of seawater and brine droplets as compared to pure water (Figure 2.8). Also, at $-30\text{ }^{\circ}\text{C}$, the retraction ratio of pure water droplets decreases substantially when compared to $-20\text{ }^{\circ}\text{C}$. At $-40\text{ }^{\circ}\text{C}$, all three solutions show zero liquid repulsion upon droplet impact (Figure 2.9); however, the retraction profiles (Figure 2.8) are different, with brine droplets retracting the most. Additionally, at $-40\text{ }^{\circ}\text{C}$, the retraction ratio of the seawater droplets decreased significantly compared to that at $-30\text{ }^{\circ}\text{C}$. For brine droplets, the retraction ratio decrease was not as large as that of the seawater droplets.

Figures 2.8 and 2.9 can be used to make conclusions regarding the utility of superhydrophobic surfaces for saltwater icephobicity applications. It is seen that superhydrophobic surfaces will display saltwater repellency at lower temperatures than those with pure water. While superhydrophobic surfaces are unable [35] to repel pure water at temperatures below $-20\text{ }^{\circ}\text{C}$, they can still repel saltwater at temperatures below $-30\text{ }^{\circ}\text{C}$, i.e., both the retraction ratio and fraction of droplet volume repelled is greater for saltwater and brine droplets. This increases the useful working temperature range of superhydrophobic surfaces in marine conditions. The addition of salt reduces the sluggishness in droplet retraction at lower temperatures. Higher retraction with saltwater or brine will thus reduce the contact area and decrease the ice-surface adhesion for ice removal applications. Overall, it can be concluded that superhydrophobic surfaces will show moderately improved performance at preventing saltwater from freezing upon impact compared to pure water.

The rest of this chapter discusses plausible mechanisms that can explain the greater bounciness of saltwater droplets. The ability of a droplet to successfully come off the surface after impact depends on the rate at which energy is lost during droplet spreading and retraction. Sources of droplet energy loss include viscous losses at the

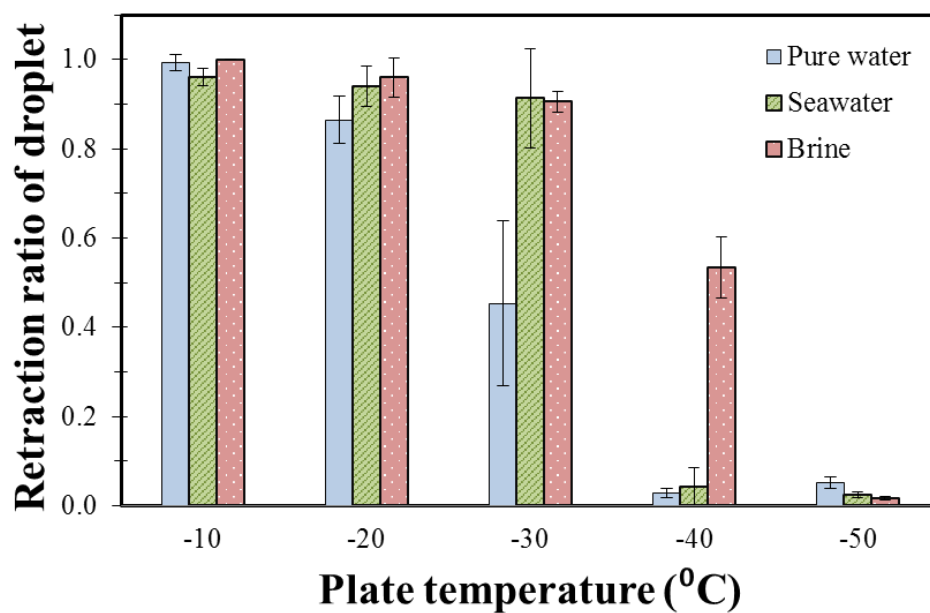


Figure 2.8. Retraction ratio corresponding to droplet impact of three liquids on a superhydrophobic surface at various temperatures.

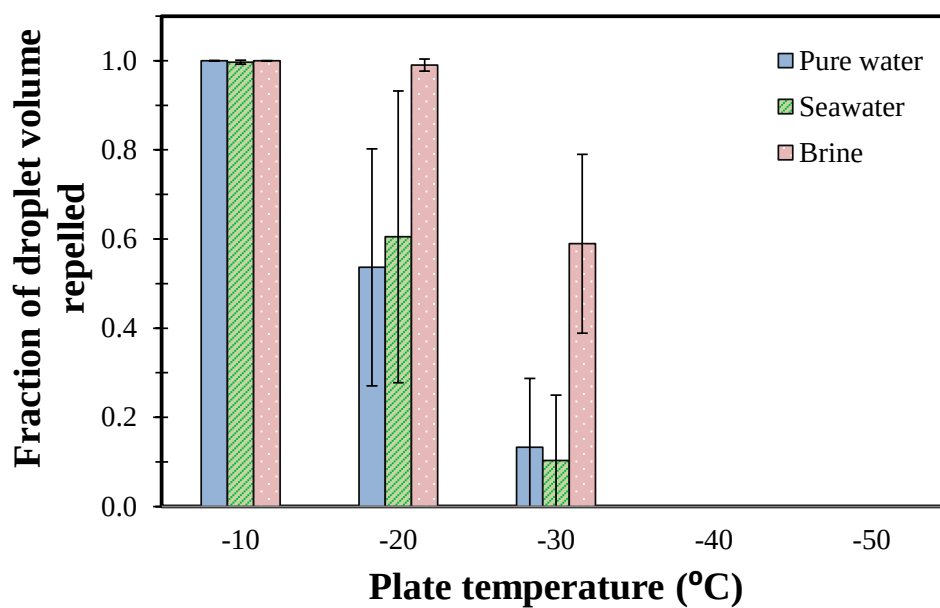


Figure 2.9. Fraction of liquid repelled after droplet impact of three liquids on a superhydrophobic surface at various temperatures.

fluid-solid interface [39, 122], contact line friction, and losses due to substrate deformation [123]. These effects are analyzed to estimate their contribution in explaining the differences in the icephobicity of saltwater droplets.

Estimating the viscous losses during droplet impact is not straightforward due to the complex fluid mechanics involved. To a first order, the viscous loss during droplet impact can be approximated as [122, 123]:

$$Viscous\ Loss = \frac{\pi}{3} \rho V^2 \frac{d_o d_{\max}^2}{\sqrt{Re}} \quad (2.2)$$

where ρ is the density, V is the impact velocity, d_o is the initial diameter, $d_{\max}$ is the maximum diameter, and Re is the Reynolds number, defined as $\frac{V d_o \rho}{\mu}$, where μ is the dynamic viscosity. The viscous loss scales as $(\rho \mu)^{1/2}$ for droplets with the same diameter and impact velocity.

However, the viscosity and density for saltwater are not very different from pure water, as shown in Table 2.2 [124]. Even though viscous losses increase at lower temperatures, this cannot completely explain the differences in the retraction between saltwater and pure water droplets. This observation is further confirmed by estimating the fraction of the droplet that sees a viscosity change with temperature. The thermal penetration depth is a measure of the distance in the liquid that the effect of the cold surface is felt. Since viscosity increases at lower temperatures, a larger penetration depth will translate to larger viscous losses and a more rapid energy loss. The thermal penetration depth scales as $\sqrt{\alpha t}$, where $\alpha = \frac{k}{\rho C_p}$ is the thermal diffusivity, t is time, k is the thermal conductivity, ρ is density, and C_p is the specific heat. However, the estimated thermal penetration depths are approximately the same for all three fluids in this study as the properties do not change significantly, as shown in Table 2.2.

Table 2.2. Thermal properties of pure water and salt solutions at 20 °C and 4 °C.

ρ (kg/m ³)				μ (mPa s)			
Temp. (°C)	Water [125]	Seawater [124]	Brine [124]	Temp. (°C)	Water [125]	Seawater [124]	Brine [124]
20	998	1024	1147	20	1	1	1.42
4	1000	1027	1150	4	1.57	1.52	2.13

C_p (J/kgK)				k (W/mK)			
Temp. (°C)	Water [126]	Seawater [124]	Brine [124]	Temp. (°C)	Water [126]	Seawater [124]	Brine [124]
20	4183	3999	3424	20	0.59	0.59	0.52
4	4211	4007	3421	4	0.56	0.58	0.51

Based on the above analyses, it is unlikely that differences in thermophysical properties are the primary reason for the difference in the impact dynamics between saltwater and pure water droplets. A more likely explanation is based on the differences in the probabilities of ice nucleation during the spreading and retraction stages. Figure 2.8 shows that all three solutions have similar retraction behavior at -10 °C; differences emerge at lower temperatures as the probability of icing increases. Clearly, pure water droplets will have a higher tendency to nucleate ice than saltwater droplets; however, ice formation and propagation will be limited in the ~ 10 ms timescale associated with droplet impact. An important consideration is the two-stage nature [12] of ice formation. Ice formation is typically broken into two stages, consisting of an initial superfast stage, followed by a much slower second stage. In the first freezing stage [12], the entire liquid mass becomes cloudy and establishes the scaffolding on which the remainder of the water solidifies. The second stage is much slower and involves propagation of the freezing front from the bottom of the droplet to the top.

The differences in the impact dynamics of saltwater and pure water are attributed to the differences in the propagation rates of the initial stage. It is known that the presence of salt and impurities slows down the initial freezing stage because the impurities must be excluded from the ‘frozen’ crystal structure [12]. This implies that the pure water droplet sees a much larger penetration of the first freezing stage than saltwater droplets during the time that the droplet contacts the surface. The initial freezing stage affects the interfacial and liquid properties since the liquid changes to a semi-solid mushy state. The resulting increase in the resistance to fluid motion hinders the retraction of pure water droplets, which can explain the differences with saltwater droplets.

This hypothesis was verified by measuring propagation velocities of the initial freezing stage in static pure water and saltwater droplets. High-speed imaging at 4000 fps was employed for these experiments. Figure 2.10 shows images of the three droplets at the time instant corresponding to approximately half way through the first freezing stage. Table 2.3 shows the average freeze times and the propagation velocities for the three liquids.

Table 2.3. Duration of initial freezing stage and propagation velocity during the initial freezing stage in three liquids.

	Duration of initial freezing stage (ms)	Propagation velocity during initial freezing stage (mm/ms)
Pure water	12.7	0.28
Seawater (0.6 M NaCl)	69.4	0.045
Brine (3 M NaCl)	1720	0.002

It is seen that the propagation velocities in saltwater are much lower than

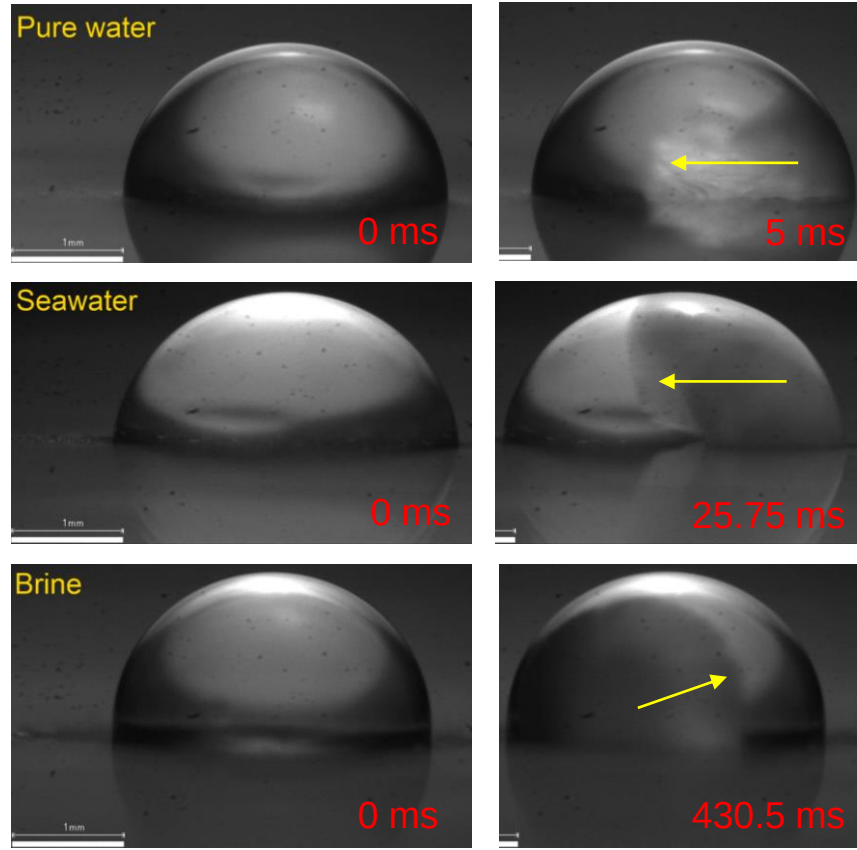


Figure 2.10. Stage-one freeze propagation in pure water, seawater, and brine. The arrows indicate the edge and direction of the moving front. The freeze front propagation velocity reduces with an increase in salt concentration.

pure water; furthermore, the propagation velocities decrease nonlinearly with the salt concentration. The initial freezing stage is slower in brine by 140X compared to pure water. This implies that most of the brine droplet will not be affected by the initial freezing stage during its residence time on the surface; this reduces energy loss in the brine droplet, allowing greater retraction. On the other hand, the timescale for the initial freezing stage in pure water is comparable to the droplet residence time; this implies that there is significant freezing (first stage) in the pure water droplet during retraction, which explains its sluggishness. It is noted that high-speed visualization to

detect freezing is not possible under droplet impact conditions due to the difficulties in distinguishing the first-stage freezing front from fluid movement.

The above hypothesis represents a plausible mechanism for the differences in the retraction characteristics of different fluids. Other effects, such as viscous losses and contact line friction, will also influence droplet impact dynamics of saltwater solutions. Overall, the lower freezing probability (due to lower freezing temperatures) and slower freeze propagation rates make saltwater droplets bouncier than pure water droplets.

2.3 Conclusions

This chapter presented a fundamental investigation of the differences in the freezing characteristics and impact dynamics of saltwater droplets. It is seen that surface chemistry does not directly affect the freezing temperature of static saltwater droplets. The impact dynamics of saltwater droplets are also different from pure water droplets; saltwater droplets demonstrate more retraction and repulsion. These results imply that existing superhydrophobic surfaces will be more effective at preventing saltwater impact icing than freshwater impact icing. This study also highlights the significant variations in the freezing rate of various saltwater solutions; knowledge of the freeze propagation rates is of critical importance in the development of applications such as freezing desalination. While the present results are based on single droplet studies, parameters, such as droplet size and droplet-droplet interaction, are also important considerations.

Chapter 3

Effect of interfacial electric fields and currents on ice nucleation in supercooled water droplets¹

In this chapter, the effects of an electrowetting electric field on the elevation of the freezing temperature of water droplets (Objective 2) are presented. The experimental setup in this work is similar to that of electrowetting, wherein a dielectric layer between the electrodes and water prevents DC current flow. Using this configuration, a series of experiments were conducted to isolate the role of surface charge and polarity on the average freezing temperature of supercooled water droplets. Ultra-high electric fields of up to $80 \text{ V}/\mu\text{m}$ were applied, which is one order of magnitude higher than in previous studies [16]. Additionally, by intentionally allowing tiny pinholes through the dielectric layer, the influence of electric current and subsequent secondary phenomena were observed. The results facilitate an in-depth understanding of various mechanisms underlying electrofreezing of water.

3.1 Experimental methods

The effect of an electric field on freezing was isolated by preventing current flow; this was achieved by using a dielectric layer between the droplet and the underlying electrode (as per the standard configuration used for electrowetting experiments [127–132]). Figure 3.1 shows a schematic of the basic setup, where a thin wire elec-

¹Material from this chapter has been published: Carpenter, K., and Bahadur, V., 2015. “Electrofreezing of water droplets under electrowetting fields.” *Langmuir*, **31**, pp. 2243–2248.

trode immersed in the droplet biases the droplet. The bottom surface is the dielectric layer with a grounded metal layer below it. The applied voltage is entirely expressed over the dielectric layer, which is much more insulating than water. There is no electric field inside the water; however, there is a strong concentrated electric field in the dielectric layer and a buildup of surface charge at the liquid-dielectric interface.

The dielectric layer prevents DC current flow; therefore, any electrofreezing effects can be attributed to the near-surface electric field alone. It should be noted that an electrical double layer (EDL) [133] will also form at the surface. However, the capacitance of the nanometer-thick EDL is significantly higher than that of the dielectric layer; the overall interfacial capacitance is the same as the dielectric layer capacitance. All experiments were conducted using DC voltages. The conditions of zero electric field inside the liquid and no current would be invalid for AC voltages.

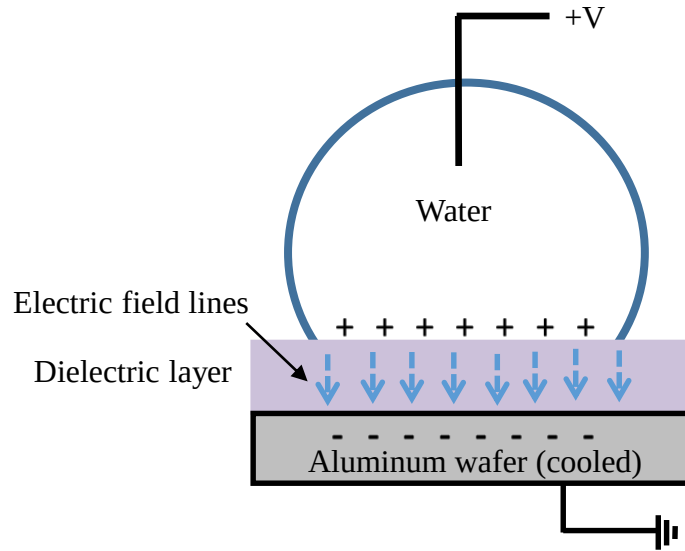


Figure 3.1. Schematic of the experimental setup to study surface electrofreezing at the solid-liquid interface.

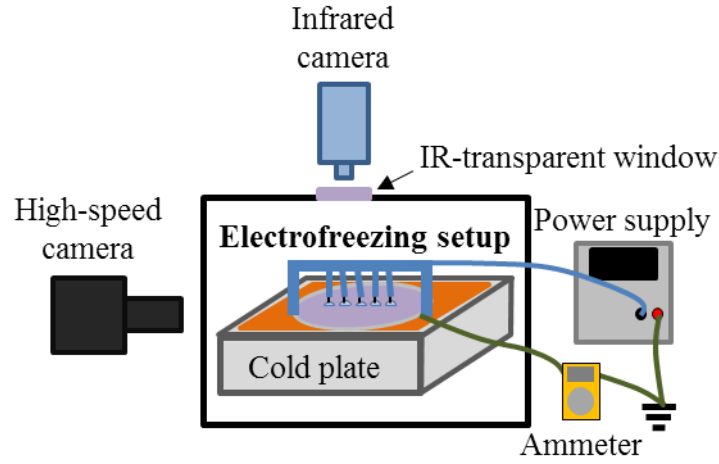
As noted in §1.2.2, the majority of electrofreezing studies used two bare electrodes immersed in the fluid [59, 60, 62, 63, 134], as shown in Figure 1.7(a). In such a configuration, numerous secondary phenomena can occur, all of which can affect nucleation, and are mentioned in Figure 1.7(a). Other electrofreezing studies have removed the possibility of current flow by suspending the positive electrode above fluid droplets [16, 45, 46, 64]. Figure 1.7(b) shows such a setup; note that these studies did not apply electric fields greater than $6 \text{ V}/\mu\text{m}$ due to air ionization and did not observe any freezing temperature elevation effect.

3.1.1 Experimental setup

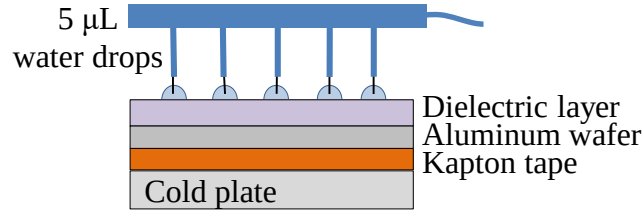
Figure 3.2 shows a schematic of the present experimental setup, and Figure 3.3 shows a photograph of the actual setup. All experiments were conducted in a custom-built environmental chamber with humidity control. The same environmental chamber and cold plate that was described in Chapter 2 was used. DC voltage was supplied by a power supply (Kepco model BHK 2000-0.1MG or Matsusada model RG-650-0.1).

The IR camera was used to measure the temperature-time history of the droplets. The high-speed camera was placed behind one of the side walls of the environmental chamber, where a glass window was installed. Additional details of the setup and equipment are provided in Chapter 2.

The temperature uniformity of the cold plate was verified by the IR camera. The cold plate was covered by black electrical tape ($\epsilon = 0.95$). The cold plate was then allowed to reach steady state at various temperatures. The temperatures of nine locations distributed throughout the area of interest were then recorded by the IR camera. It was found that the temperatures were within 1°C of each other.



(a)



(b)

Figure 3.2. Schematic of experimental setup. a) Environmental chamber and b) Electrofreezing setup.

The accuracy of the IR temperature measurements and plate temperature was verified using a high-accuracy thermometer (Fluke Model 1523, readout with a precision thermistor probe). The reference thermometer readout and the thermistor probe were calibrated as a pair by the manufacturer (combined uncertainty of ± 0.013 °C). An aluminum block with a hole bored through the middle was used. The thermistor was placed in this hole, and the aluminum block was placed on the cold plate. Black electrical tape was placed around the aluminum block on the cold plate. IR temperatures were recorded on the black tape on the cold plate. The differences between the

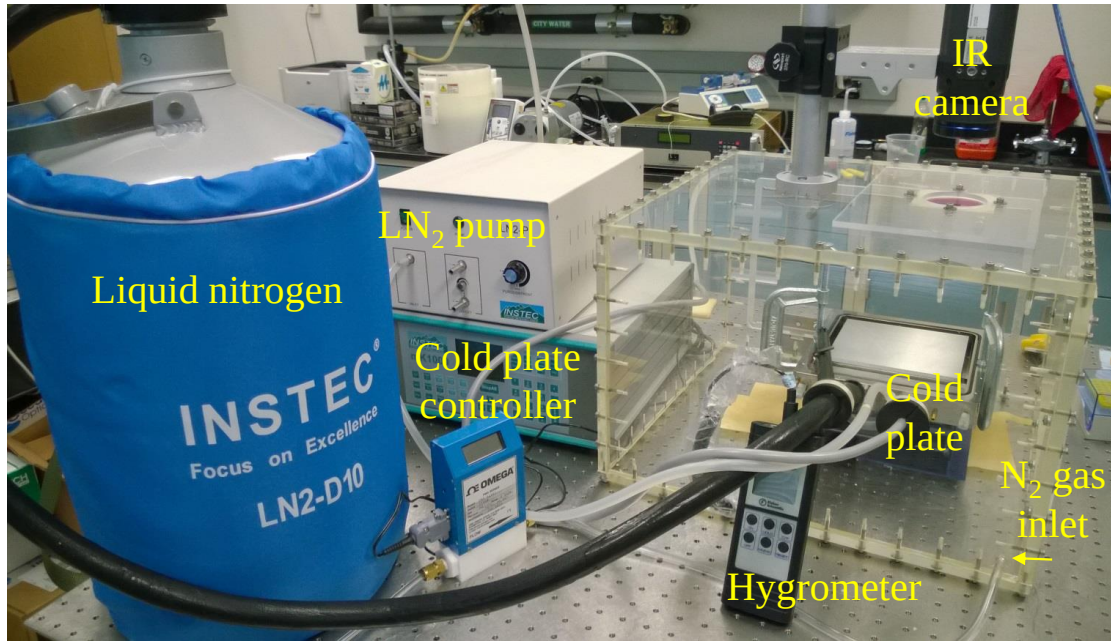


Figure 3.3. Photograph of experimental setup used for studies on electrofreezing.

plate temperature and the thermistor were less than 0.4 °C. The differences between the thermistor reading and IR camera measurements were between 1-1.5 °C.

Figure 3.2(b) shows details of the electrofreezing setup, which involves water droplets manually deposited on a dielectric layer. The dielectric layer is attached on top of an aluminum wafer (diameter of 100 mm, thickness of 0.8 mm). The aluminum wafer was attached to the cold plate using thermal grease, and a layer of Kapton tape was used between the wafer and the plate to protect the cold plate from current leakages.

Thin (diameter of 0.25 mm) wires were inserted into the droplets to bias them, and the ground wire was attached from the aluminum wafer to the ground of the power supply; both wires were then connected to the building ground.

In this study, two dielectric surfaces were tested, 25- μm thick polyimide film (Kapton from DuPont) and CYTOP (Asahi chemicals). Each experiment involved five droplets; these droplets were biased using five wires (diameter of 0.25 mm, tin-plated copper) connected to the power supply. The five wires were positioned using an acrylic holder, as shown in Figure 3.2(b). In this way, five droplets could be tested simultaneously. At each voltage, experiments were repeated at least twice.

3.2 Experimental procedure

For each experiment, 5 μL deionized (DI) water droplets ($\epsilon = 0.98$) were deposited on the dielectric surface, and the wires were carefully positioned within the droplets. The chamber was flushed with nitrogen gas to reduce the humidity. Experiments began once the hygrometer read a humidity of less than 1%. The total time between when the chamber door closed and when an experiment began was less than two minutes.

For every experiment, the initial plate temperature was 10 $^{\circ}\text{C}$, which was set once the hygrometer read 30% to avoid any condensation on the plate. Once $<1\%$ humidity was reached, the infrared camera began recording. If voltage was applied to the droplets, the power supply was then turned on, and the plate was set to cool at a rate of 5 $^{\circ}\text{C}/\text{min}$. Note that wires were inserted into the droplets even for the 0-V experiments. Experiments ended once all the droplets had frozen, which could be visually verified when the droplets changed from clear to opaque.

3.3 Data analysis

The IR camera measured the temperature at the top of the droplet. A more appropriate temperature to better describe freezing is the interface or surface tem-

perature between the droplet and the dielectric layer. A simplified 1-D analysis was conducted to estimate the surface temperature from the measured droplet temperature. With a knowledge of the droplet temperature measured by the infrared camera, the plate temperature, and the thermal conductivities and lengths of the Kapton tape, aluminum wafer, dielectric layer, and water droplet, the surface temperature can be estimated as per the details provided in Appendix A.

The onset of ice nucleation is identified by a rapid temperature increase, which is due to the release of latent heat when the liquid droplet solidifies. The freezing temperature is then estimated as the interface temperature (see §2.1.1). The error bars were calculated using the t-value and a 95% confidence interval, as defined by Eqn. 2.1.

3.4 Influence on electric fields on freezing temperature

Figure 3.4 shows the electrofreezing curve (freezing temperature versus the electric field) for the polyimide film. Note that each data point is the average of 10 freezing temperature measurements. It should be noted that a new layer of polyimide was used for each experiment to ensure cleanliness.

It is clearly seen that electric fields elevate the freezing temperature for both positive and negative polarities at the fluid-solid interface. In the absence of an electric field, the DI water droplets freeze at approximately $-30\text{ }^{\circ}\text{C}$, which is expected because there are no external stimuli, such as vibrations or air drafts, to trigger nucleation in the stationary supercooled droplets. With increasing electric fields, the droplets freeze at higher temperatures. There is a sharp increase in the freezing temperature for electric fields up to $20\text{ V}/\mu\text{m}$. However, the electrofreezing effect saturates thereafter, and greater electric fields result in a marginal freezing temperature elevation. Overall,

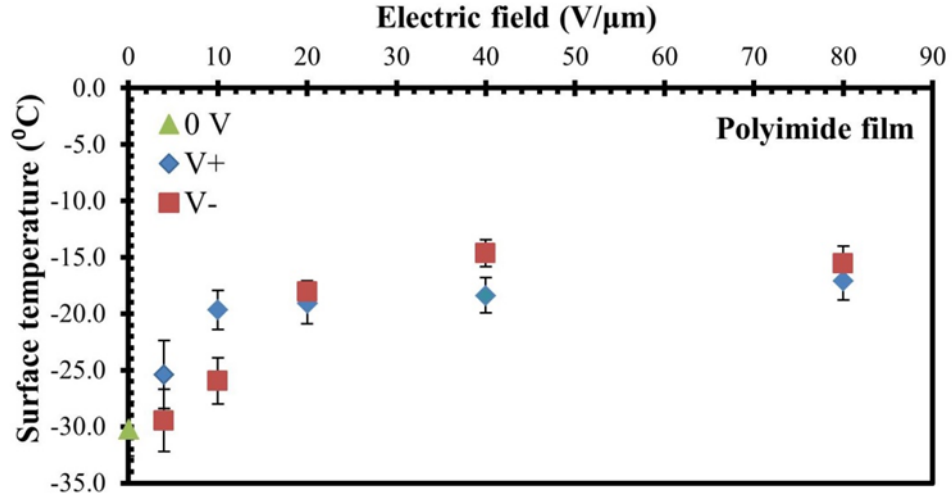


Figure 3.4. Electrofreezing curve for polyimide film. It is seen that the electrofreezing effect saturates for fields stronger than 20 V/μm.

it was seen that electrofreezing can elevate the freezing temperature by more than 15 °C, which is significant for many applications. It should be noted that the magnitude of the electrofreezing effect will also depend on the geometry and fluid volumes, and the present results should not be assumed to be representative of all electrofreezing situations.

It is important to note that the effect of polarity on the electrofreezing effect was observed to be insignificant. Below 10-V/μm electric fields, positive surface voltages resulted in greater temperature elevations than negative voltages. However, this appears to be a secondary effect because both polarities display the same trend and nearly the same electrofreezing temperatures at higher electric fields. The nature of the ions at the surface will affect the local energy barrier for nucleation; however, the present results suggest that polarity and surface chemistry-based factors are less important than the strength of the electric field.

It should be noted that extremely high electric fields ($80 \text{ V}/\mu\text{m}$) were used in these experiments, which are an order of magnitude higher than that reported in literature. However, these fields were still below the breakdown strength of the dielectric materials, which is $\sim 300 \text{ V}/\mu\text{m}$ for polyimide. Another important aspect of this work is that every sample was used for only a single experiment. It is a well-documented observation that dielectric layers can degrade or trap charges with repeated use at high voltages. To avoid confounding the present results with such phenomena, it was decided to use a dielectric layer for one experiment only. It should also be noted that the footprint area of the droplet will change with the applied voltage due to the electrowetting effect. However, this area increase occurs before the droplet freezes and will not affect the electrofreezing trends.

The mechanism of surface electrofreezing can be attributed to the presence of an electric field-induced charge at the surface; however, the effect of surface polarity was not seen to be significant, unlike in the work of Ehre et al. [47]. This leads to the conclusion that the electric-field-induced change in the activation energy to overcome the nucleation barrier is the mechanism for the temperature elevation. This can be explained using classical nucleation theory with an additional capacitive energy term. The initiation of a seed nuclei requires the net Gibbs free energy to be negative. The net Gibbs free energy for ice nucleation involves a term corresponding to the energy required to create the solid-liquid interface and a volumetric term corresponding to the latent heat release. In the presence of electric fields, the water-ice conversion also changes the electrical energy stored in the dielectric capacitor below the droplet, which is captured by an additional electrostatic term. The resulting Gibbs free energy

change can be represented as:

$$\Delta G_{\text{ef}} = V_{\text{ice}}\Delta G_{\text{ice}} + A_{\text{ice-surface}}(\gamma_{\text{ice-solid}} - \gamma_{\text{water-solid}}) + A_{\text{ice-water}}\gamma_{\text{ice-water}} - \frac{1}{2}A_{\text{ice-surface}}k_{\text{ice}}\epsilon_0\frac{V^2}{t_{\text{ice}}} \quad (3.1)$$

where ΔG_{ef} represents the Gibbs free energy change for electrofreezing, V_{ice} represents the volume of the seed ice crystal, ΔG_{ice} represents the energy release due to ice formation, A represents various areas, γ represents interfacial energy, k_{ice} is the dielectric constant of ice, ϵ_0 is the permittivity of a vacuum, t_{ice} is the thickness of the ice crystal, and V is the applied voltage. It should be noted that accurate estimates of the dielectric constant and size (thickness) of the ice crystal at the critical radius are not available. In particular, it is challenging to quantify the critical nucleus size; a recent molecular dynamics study indicates that this size itself depends on the electric field strength [135]. Quantitative analyses based on Eqn. 3.1 have therefore not been presented. However, Eqn. 3.1 does qualitatively capture the energetics of the formation of an ice crystal on the solid-liquid interface in the presence of an electric field. The electrostatic energy term reduces the energy barrier for nucleation, which explains the increase in freezing temperatures at higher electric fields. It should be noted that molecular dynamics studies suggest that electric fields reorient water molecules into a favorable configuration for nucleation at very high field strengths ($\sim 1000 \text{ V}/\mu\text{m}$) [135–138]. However, such field strengths cannot be achieved in practice due to dielectric layer breakdown limitations. Recently, a study that experimented with polar crystals that exhibit pyroelectricity (a temperature change alters the bulk polarization of the material) also showed that surface charge alone has a dominant influence on heterogeneous nucleation [139].

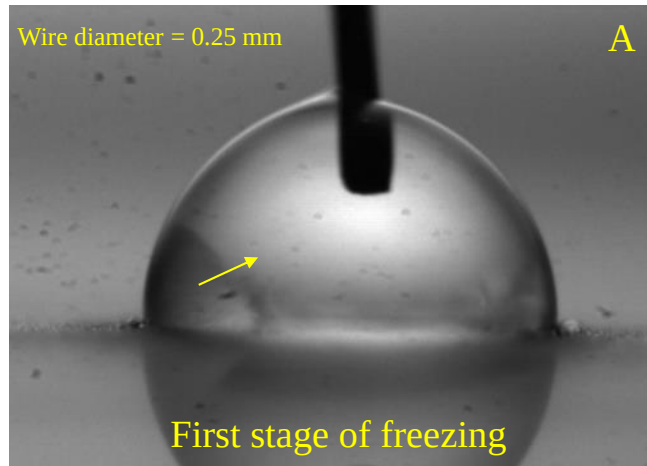
More insights into the electrofreezing process emerge from an analysis of high-speed electrofreezing visualizations. Figure 3.5 shows snapshots from a high-speed

recording of droplets freezing on CYTOP with no voltage applied. It is seen that nucleation initiated at the three-phase contact line. Note that nucleation was also observed to begin at the three-phase contact line when an applied voltage was applied. This is expected because it is the preferred nucleation site in the absence of electrical voltages. The presence of a sharp liquid wedge near the three-phase line further concentrates the electric field lines. The freezing process consists of two phases and begins with a rapid phase (Figure 3.5(a)), wherein the entire droplet converts to a gel-like state in <20 milliseconds. This stage is followed by a slower phase (Figure 3.5(b)), on the order of seconds, in which the freezing front moves from the surface to the top and ends with a completely solidified ice droplet.

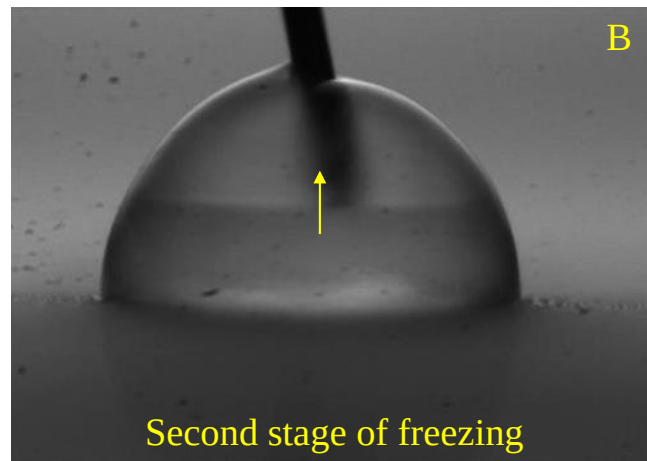
3.5 Role of electric currents on electrofreezing

This section presents experimental results to isolate the influence of electric currents on electrofreezing and highlights the complexities involved in electrofreezing experiments. These experiments were performed with CYTOP films. CYTOP is a commercially available amorphous fluoropolymer. The dielectric strength of CYTOP is $90 \text{ V}/\mu\text{m}$, and in the following experiments, the highest electric field used was $70 \text{ V}/\mu\text{m}$. The purpose of using CYTOP was two-fold: (1) to experimentally validate the previously described results obtained with polyimide films and (2) to intentionally create pinholes in the CYTOP layer to allow current flow during electrofreezing experiments.

CYTOP films were fabricated on an aluminum wafer using the following procedure. CYTOP was spincoated onto the aluminum wafer at 500 rpm for ten seconds followed by 1000 rpm for twenty seconds. The CYTOP was then soft baked on a hot plate at 120°C for approximately 5 minutes. After the final coat and soft bake, the



(a)



(b)

Figure 3.5. High-speed imaging of the two stages of freezing. Frame A is a snapshot during the rapid first stage; note that nucleation begins at the three-phase line. Frame B is a snapshot during the slower second stage of freezing, which begins from the bottom of the droplet and moves upwards. The first stage of freezing lasts for a few milliseconds, whereas the second stage of freezing lasts for seconds.

wafer was hard baked in an oven at 200 °C for 1 hour. The thickness of the final CYTOP layer was measured using a profilometer (Detak 6M Stylus).

For the CYTOP experiments, it was determined that O₂ plasma cleaning (March Plasma CS170IF RIE etching system) was required before each day of testing to ensure consistent results from day to day. The wafer was cleaned for 10 seconds at 50 W with 20 sccm of O₂. Plasma cleaning will remove CYTOP; however, it was determined that the amount of CYTOP removed after testing was less than 3%.

Figure 3.6 shows the electrofreezing curve for CYTOP, wherein the same broad trends as for polyimide films are obtained. These CYTOP films were deposited by four consecutive spin coats on an aluminum wafer to stagger any defects in the dielectric layer; the total thickness was approximately 4 μm , and no current flow was measured. Electrofreezing experiments were also conducted with two spin-coated CYTOP layers with a thickness of 2.2 μm , which allowed current to pass due to tiny pinholes in the CYTOP layers, which will be discussed shortly. Due to the larger scatter observed, more than 10 measurements were performed for certain electric field strengths. Table 3.1 lists the number of droplets tested in the CYTOP experiments. Note that an ammeter (multimeter, Agilent Technologies U3401A) was added between the ground wire from the aluminum wafer to the building ground (see Figure 3.2(a)) to measure the current.

It is seen from Figure 3.6 that much higher electrofreezing temperatures were obtained with the 2.2- μm thick CYTOP layer (with pinholes; symbol: hollow diamond) than those from the 4- μm thick CYTOP layer (no pinholes; symbol: solid diamond). Furthermore, the results on CYTOP films with pinholes show more scatter, as depicted by the error bars in the plot. Using high-speed photography, it was discovered that tiny bubbles were originating at the solid-liquid interface of the CY-

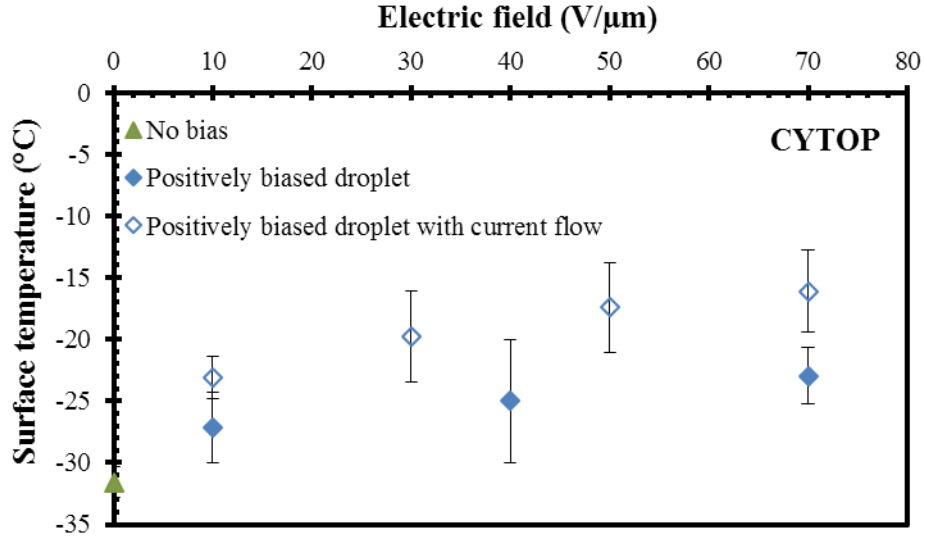


Figure 3.6. Electrofreezing curve for CYTOP in the presence and absence of current in the droplet. It is seen that current flow and chemical reactions increase the freezing temperatures and also result in more scatter in the temperature elevations.

Table 3.1. Number of droplets used in the CYTOP experiments.

With current flow		Without current flow	
Electric field strength (V/μm)	Number of droplets	Electric field strength (V/μm)	Number of droplets
0	20	0	35
+10	10	+10	10
+30	10	+40	10
+50	10	+70	25
+70	15		

TOP layer with pinholes (see Figure 3.7). These bubbles are likely the result of gas being released due to electrolysis or other chemical reactions at the surface. These bubbles also act as ice nucleation sites and are responsible for the increased electrofreezing temperatures. Bubble formation is also accompanied by measurements of small amounts of electric currents (20-100 μA), which indicates that the dielectric layer contained pinholes (see Figure 3.8). Multiple spincoats stagger defects and eliminate current leakage, which leads to lower, less variable electrofreezing temperatures (like in the 4- μm thick CYTOP layer). It should be noted that much larger datasets were collected for the experiments with bubbles because of the larger scatter observed.

The above experiment highlights the complications involved in experimental

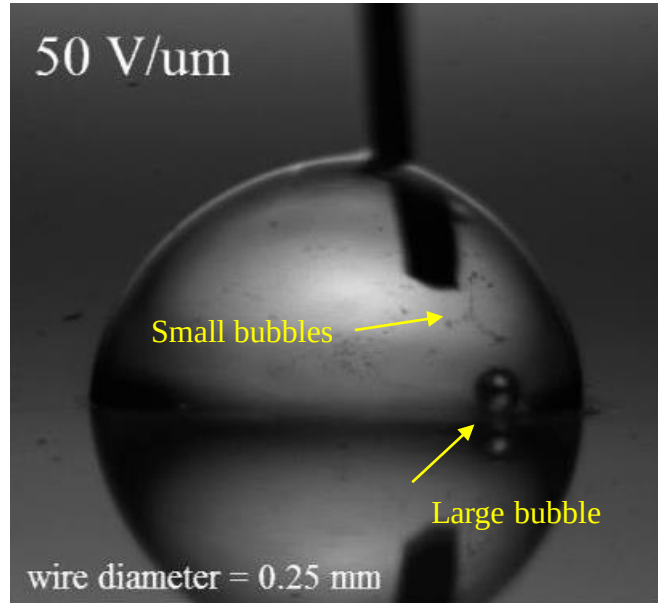


Figure 3.7. Illustration of electrolysis occurring during the electrofreezing experiment. The bubbles originate at a pinhole (located at the site of the large bubble) and travel upwards to the wire electrode.

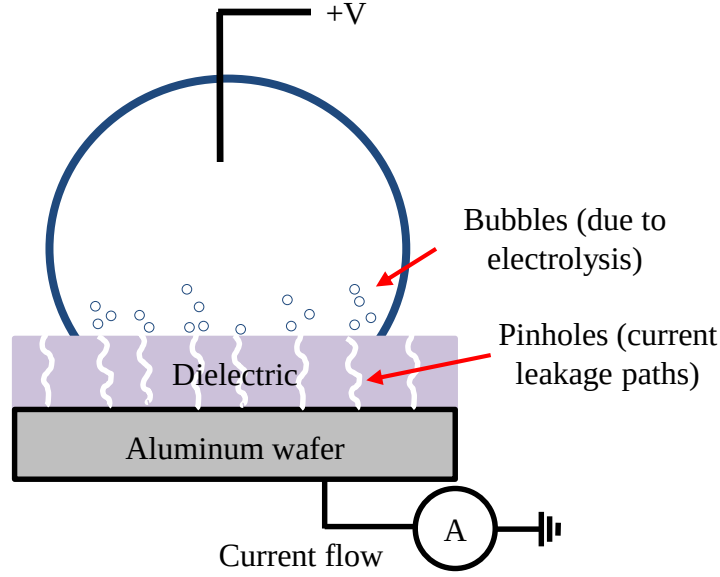


Figure 3.8. Schematic illustration of electrolysis during the experiment on electrofreezing.

characterizations of electrofreezing. Numerous past studies have intentionally passed current pulses with the objective of triggering nucleation; however, in such studies, electrofreezing cannot be attributed to only the electric field strength; the electrofreezing effect is also affected by the magnitude of the current and possible chemical reactions that simultaneously occur. Furthermore, the question of Joule heating due to current flow is a significant one that has not been addressed at all in previous literature. In the present experiments, we were able to systematically isolate the effect of the electric field from the current flow on the electrofreezing process, which is a significant advancement in the current understanding of this phenomenon.

It should be pointed out that several nucleation triggers exist in the presence of current flow and bubble generation. These include heterogeneous nucleation on bubble surfaces and fluid convection resulting from bubble growth. The effect of the electric field will also be important, though the field magnitude and distribution will

change due to current passage. Overall, it can be concluded that both electric fields and electric currents influence electrofreezing; however, the physical mechanisms are very different.

3.6 Conclusions

This chapter presented the first in-depth study of surface electrofreezing and explains the basic mechanisms underlying this phenomenon. These findings are based on investigations of the influence of the electric field, polarity, and electric current on the electrofreezing temperature.

With surface electrofreezing, the electric field is concentrated near the solid-liquid interface. The results from this work clearly show that as the magnitude of the electric field increases, the average freezing temperature also increases; however, this elevation in freezing temperature eventually saturates beyond a certain electric field magnitude. Also, at low field strengths ($< \sim 5$ V/m), the freezing temperature elevation is essentially non-existent, which has also been verified in another recent study [140]. Furthermore, it was shown that the surface polarity does not significantly affect the freezing temperature. It can therefore be concluded that the freezing temperature elevation is due to the change in activation energy, i.e., an additional electrostatic energy component in the Gibbs free energy balance reduces the energy barrier to nucleation. Heterogeneous electrofreezing can also be triggered by current flow through water; in such cases, the freezing temperatures are higher. The physical mechanisms for electrofreezing in this case are more complex and include the effects of an electric field plus the effects of bubbles, which act as nucleation sites.

Chapter 4

Rapid formation of tetrahydrofuran (THF) hydrates by electro-nucleation

The objective of the work described in this chapter is to investigate the use of electrofreezing to rapidly induce the formation of tetrahydrofuran (THF) hydrates. THF ($\text{C}_4\text{H}_8\text{O}$) hydrates are synthesized from a mixture of THF and water. THF hydrates are very commonly used [80, 111, 141–145] as model hydrates because they form at atmospheric pressures (unlike methane hydrates) and retain the same structure as many common gas hydrates.

The results of Chapter 3 demonstrated that ice nucleation can be promoted by electrowetting fields, i.e., applying a potential difference between two electrodes separated by water on a dielectric layer. It was observed that electric fields and electric current contributed to elevating the freezing temperature. The experiments presented in this chapter demonstrate the use of electrofreezing to rapidly induce formation of THF hydrates. While THF hydrates ordinarily require tens of hours to form with no voltage/current applied, this study reports a voltage/current threshold that forms THF hydrates within 10 minutes of applying the voltage. The influence of electric field and electric current on the induction time of THF hydrates is studied. Visualization of THF hydrate formation confirms the existence of a two-stage freezing process similar to that of ice formation. The results of this work suggest that this technique can enable rapid hydrate formation and overcome a significant issue associated with the development of several hydrate-based applications.

4.1 Details of experiments

This section describes two experiments that were conducted in this study: 1) constant-temperature bath experiments and 2) visualization of the hydrate freezing process.

Firstly, the influence of voltage/current on the induction time for THF hydrate nucleation was characterized in a constant-temperature bath (bath temperature is below the thermodynamic formation temperature of THF hydrates). Therefore, instead of measuring the average freezing temperature (as in Chapter 3), the amount of time that before formation is initiated, i.e., the induction time, was determined. The induction time was used to characterize the influence of the electro-nucleation effect on hydrate formation.

The constant-temperature bath setup was chosen because THF evaporates rapidly. Conducting droplet-based experiments is challenging since the THF in small droplets in a low-humidity environment will evaporate rapidly and will disrupt the THF/water ratio. Therefore, it was necessary to enclose the THF/water solution in a sealed container. This type of experimental setup is common in studies that utilize THF hydrates [94, 111, 144].

The second experimental setup was used to visualize hydrate droplet formation on a cold plate. Experiments were designed to be completed in less than 2 minutes to avoid significant mass loss due to THF evaporation.

4.1.1 Constant-temperature bath setup

Figure 4.1(a) shows an image of the constant-temperature bath setup, which primarily consists of a 15-Liter cold bath (PolyScience, EW-12210-26), power supply (Kepco, BHK 2000-0.1MG), an electrometer (Keithley 6514; 200 μ A range, accuracy

of $(0.1\% \text{ rdg} + 0.00005 \mu\text{A})$; 2 mA range, accuracy of $\pm(0.1\% \text{ rdg} + 0.0001 \text{ mA})$) to measure current, and a DAQ system connected to a PC. The cold bath contained a 50/50 mixture of water and ethylene glycol (Fischer Scientific, certified).

Glass tubes (76.2 mm long, inner diameter of 10.4 mm) were used to contain

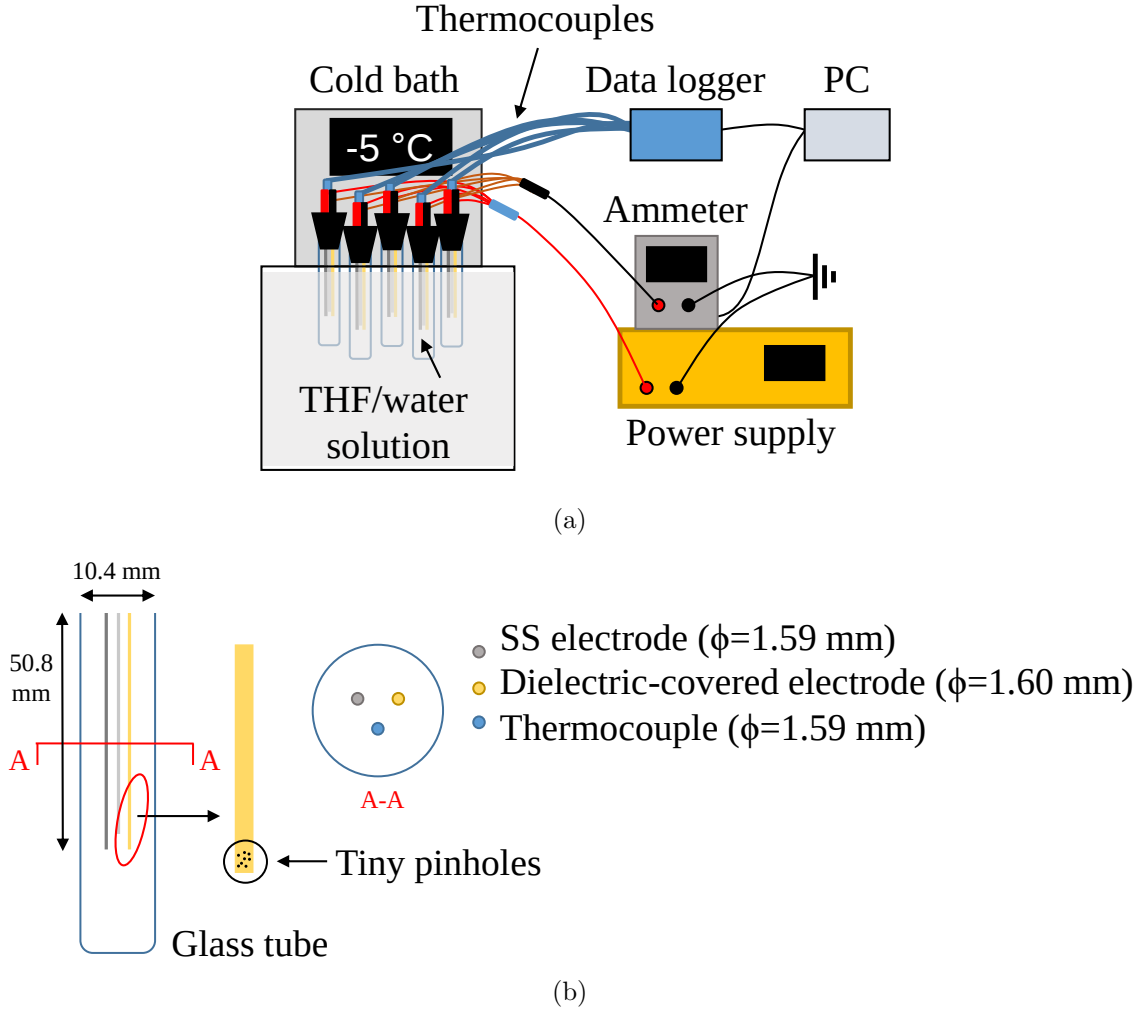


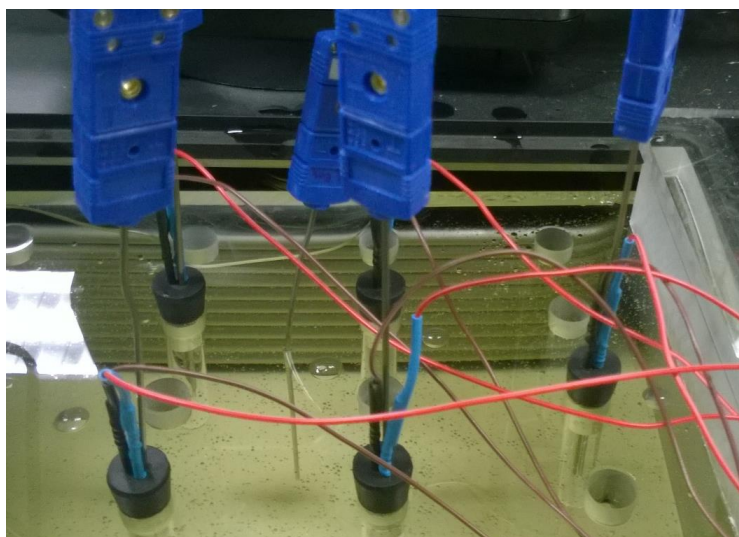
Figure 4.1. a) Schematic of constant-temperature bath setup b) Details of the electrodes inside the test tube, where tiny pinholes are created at the bottom of the dielectric-covered electrode to enable passages for current flow. Note that the electrode configuration is identical for the no-current experiments, except for the absence of pinholes.

the mixture of THF and deionized water, as shown in Figure 4.1(b). The tubes were capped with a rubber stopper to prevent evaporation. As shown in Figure 4.2, the rubber stopper seals the glass tubes and holds in place two stainless steel electrodes (McMaster, 1.59 mm diameter) and an ungrounded Type-T thermocouple (1.59 diameter, ± 1 °C). The distance between the end of the stopper and the tips of the electrodes/thermocouple was 50.8 mm. The spacing between the electrodes and thermocouple was approximately 1.25-1.5 mm. An acrylic holder was machined to allow the glass tubes to be immersed in the bath. Note that an ungrounded thermocouple was chosen to prevent the applied electrofreezing voltage from influencing the thermocouple temperature readings.

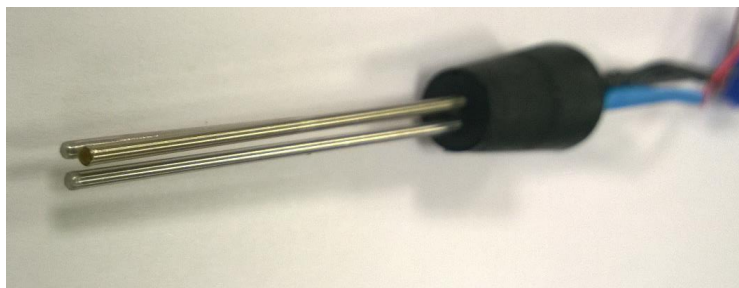
4.1.1.1 Preliminary experiments to finalize electrode configuration

The final electrode configuration, which is described in the next section, was chosen after preliminary proof-of-concept experiments with several electrode configurations. Magnet wire was used as the electrode in one of the early experiments. Magnet wire consists of a copper wire that is coated with a thin layer of insulation to prevent current flow. At the tip of the wire, however, the copper wire is exposed. This provides a controlled pathway for current flow, which was desirable for these experiments. However, it was found that after applying voltage, copper oxide would form at the tip of the ground electrode, which ultimately prevented current flow. For these reasons, magnet wire was not used in further electro-nucleation experiments.

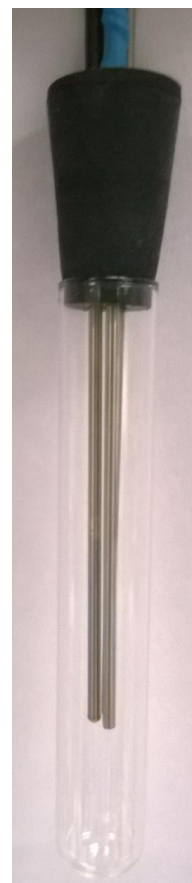
Next, stainless steel electrodes were chosen due to their inertness. The ground electrode was covered with CYTOP, which is one of the dielectric materials used in the electrofreezing work described in Chapter 3. To create current pathways, 5 horizontal cuts were made on the dielectric, which were distributed evenly vertically along the



(a)



(b)



(c)

Figure 4.2. a) Image of test tubes (with electrodes) immersed in the cold bath: red wires are connected to the power supply. Brown wires are connected to the building ground. b) Close-up image of the two electrodes and thermocouple probe. c) The two electrodes and thermocouple are held in place by a black rubber stopper. The rubber stopper seals the glass tube.

ground CYTOP-covered electrode. Preliminary results showed that voltage-induced current flow produced small streams of tiny bubbles (due to electrolysis). Eventually, many of these streams would cease to flow; in their place, larger bubbles appeared at the site of the cut, and the current would be lower than its initial value since the large bubbles reduce current flow. Despite the numerous stagnant bubbles on the

electrodes and thermocouples, nucleation was not observed to occur more rapidly. However, there was evidence that nucleation was triggered faster when the small bubble streams were present.

The above experiments suggested that smaller cuts (current pathways) were needed to allow bubble streams to flow continuously and avoid bubble coalescence into larger, stagnant bubbles. This observation significantly informed the final designs described in §4.1.1.2, where ground electrodes were fabricated with many tiny pinholes concentrated at the tip of the electrode.

Also, it is noted that the aforementioned preliminary experiments were conducted at a constant bath temperature of 1 °C, which is higher than the constant bath temperature experiments described later in this chapter. The decision to lower the bath temperature was to allow more experiments within a given time period.

Additionally, these preliminary experiments showed that suddenly increasing or decreasing the voltage level could induce hydrate formation within minutes of the increase/decrease. However, the effect of pulsing voltages was not explored in detail in this work. This observation is extremely significant and should be a point of investigation in the future.

4.1.1.2 Electrode fabrication

For each glass tube, one of the electrodes (henceforth referred to as the anode) was connected to the positive connection of the power supply, whereas the other electrode (henceforth referred to as the cathode or ground electrode) was connected to the building ground, which was also connected to the ground connection of the power supply. Both the anode and cathode electrodes were made of the same stainless steel; however, the cathode was coated with a dielectric material (CYTOP, Asahi

chemicals).

To create both the anode and the cathode electrodes, the stainless steel (SS) rods were first cut to size (10.1 cm in length). To remove any sharp grooves or cuts at the electrode ends, both ends of the electrodes were filed down with a file until smooth. The edge along the diameter of each end was also filed to remove any sharp edges. Afterwards, the electrodes were cleaned by sonicating in acetone, isopropanol alcohol, and deionized water each for 5 minutes to remove any particles and grease.

To prepare the cathode, the SS rods underwent a 4-coat dipcoating process, where CYTOP was used as the coating. Four coatings were necessary to ensure that pinholes created during the fabrication process were staggered. After cleaning and drying in a custom-made copper oven at 115 °C for 10 minutes, the electrodes were allowed to cool before being dipcoated slowly into the CYTOP solution, which had been thoroughly degassed to ensure that no air bubbles were present. The degassing process was as follows: in a glass tube, CYTOP was degassed by switching between sonication in a water bath and being placed in a dessicator until bubbles ceased to form.

Excess CYTOP was allowed to drip off the electrode before being placed in a 120 °C oven for 5 minutes to softbake. After cooling for about a minute at room temperature, the electrode was again dipcoated. This process was repeated for a total of four coats. After the last coat, the oven was heated to 200 °C, and the electrodes were hardbaked for 1.5 hrs. The final thickness of the dielectric layer was approximately 0.01 mm, which was determined using calipers. It is noted that despite the four coats of CYTOP, small amounts of current flow was still observed. The current was negligible and not factored in the present analysis (at 100 V, current was less than 2 μ A for each individual set of electrodes).

The anode, cathode, and thermocouple were inserted into three separate holes that had been carefully drilled into the rubber stopper. Wires were attached to both electrodes by wrapping the wire around the ends of the electrodes, which were then completely covered and held in place with heat shrink material.

Two sets of cathode electrodes were created: a set of 5 electrodes with pinholes (to allow current to flow between electrodes under an applied voltage) and a set of 2 electrodes without pinholes (to ensure no current passage even when voltage is applied). In the cathode with pinholes, 40 pinholes were created using the tip of a new razor blade; these pinholes were located towards the end of the electrode and distributed approximately equally around the circumference of the electrode, as shown in Figure 4.1(b). Note that an ungrounded thermocouple was chosen to prevent the applied electrofreezing voltage from influencing the thermocouple temperature readings.

4.1.1.3 Solution preparation and cleaning procedures

The chemical formula for THF is C_4H_8O , and it forms structure II hydrates, which is also the structure of many common gas hydrates [76]. The stoichiometric molar ratio between THF and water is 1:17 (i.e., 17 water molecules per THF molecule, mass ratio consists of 81% water). The formation temperature for THF hydrates is ~ 4.4 °C at atmospheric pressure. In this work, a molar ratio of 1:15 was used to ensure that only THF hydrates form; it has been shown that when a 1:17 ratio (THF:water) is used, a mixture of both ice and THF hydrate is generally obtained [80]- a slight excess of THF ensures that only THF hydrates form. THF was purchased from Sigma-Aldrich (99.9% purity), and deionized water was purchased from McMaster. The total liquid volume in each glass tube was 5 mL. After the solution of

THF and water was prepared and mixed via vigorous shaking, the tube was capped and degassed for 10 minutes in a sonication bath (Branson 2800).

After each experiment, the electrodes/thermocouple and the glass tubes were cleaned. The electrodes/thermocouple were first wiped with acetone soaked in a kimwipe followed by sonication in a bath. The electrodes/thermocouples underwent three separate sonication treatments for cleaning, each for 5 minutes, where glass tubes with the electrodes/thermocouple were filled in succession with acetone, isopropanol alcohol, and then deionized water. Glass tubes were also cleaned with a similar procedure by sonication, though in the first step, the glass tubes were filled with soapy water and sonicated, then thoroughly rinsed with tap water, followed by 5 minutes of sonication in acetone, isopropanol alcohol, and deionized water in succession.

4.1.2 Experimental setup for visualization of hydrate formation in droplets

Because hydrate formation in the glass tubes could not be directly observed while immersed in the cold bath, hydrate formation was visualized using the environmental chamber, cold plate setup, and high-speed camera described in §2.1.1.

As shown in Figure 4.3, a top-view camera angle was used to visualize hydrate freezing using the high-speed camera and a macro lens (Tokina, AT-X M100 Pro D). In these experiments (similar to the experimental setup of Figure 3.2), a polyimide film (thickness of 0.5 mil) was used as the dielectric layer, which covered an aluminum wafer (diameter of 100 mm, thickness of 0.8 mm) resting on the cold plate. A wire connected to the aluminum wafer was connected to the building ground. A 0.25-mm diameter tin-plated copper wire was connected to the positive terminal of the power supply and contacted the top of the droplet. To allow current flow, a single

small hole was created through the polyimide film using a needle. 100 V was used in all experiments conducted with this setup. It should be noted that unlike in the experiments in Chapters 2 and 3, the environmental chamber was not flushed with nitrogen. This change was done to enable a quick experiment in view of the high evaporation rates of THF.

4.2 Experimental procedures

4.2.1 Experimental procedures for constant-temperature bath setup

The bath temperature was initially set at 5 °C. The glass tubes with a solution of 1:15 THF/water were placed in the bath, and the thermocouples and wires were connected to the DAQ and power supply/ground, respectively. The temperature of each tube was allowed to come to steady state, which is defined as experiencing a less than a 0.01 °C temperature deviation for 5 minutes. A LABVIEW program contin-

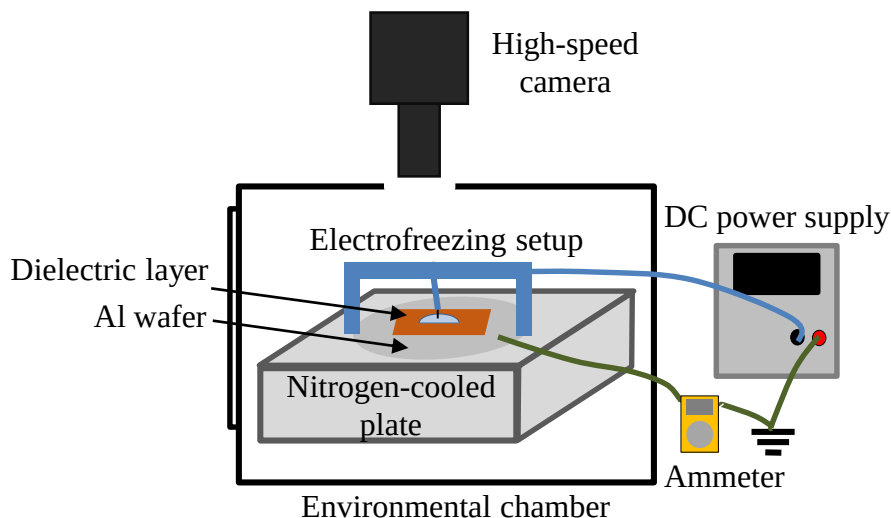


Figure 4.3. Schematic of experimental setup to visualize the kinetics of THF hydrate formation.

uously recorded the temperature, and an excel macro provided by the electrometer manufacturer recorded the current every 5 seconds. After reaching steady state, the LABVIEW program and excel macro began to record the temperature of each thermocouple and current, respectively. The bath temperature was next set to $-5\text{ }^{\circ}\text{C}$. The thermocouples reached $-5\text{ }^{\circ}\text{C}$ after approximately 20 minutes. For the experiments with voltages, the voltage was turned on at the 20-minute mark.

Three types of experiments were conducted: 1) with voltage and current flow, 2) no voltage (and therefore no current), and 3) with voltage but no current. In the voltage/current experiments, four voltages were applied (10, 25, 50, and 100 V). In the voltage/current experiments and no-voltage experiments, five glass tubes were used for one experimental run using the five electrodes with pinholes. The second set of electrodes with no pinholes were used in the experiments with voltage but no current, where two glass tubes were run simultaneously.

Induction time is defined as the interval required to form the very first hydrate cluster that is large enough for spontaneous further growth [83]. In this study, the induction time is defined as the time interval from when the thermocouples reach $-5\text{ }^{\circ}\text{C}$ to the time when hydrate nucleation is detected via a temperature spike (detected by the thermocouple). This temperature spike signals the release of heat associated with THF hydrate formation.

In such experiments, it is possible that ice can be formed instead of THF hydrates. The temperature-time curve (Figure 4.4) can be used to conclude that THF hydrates (and not ice) was being formed. Figure 4.4 shows the curves for five glass tubes. Three glass tubes were filled with water, and two glass tubes were filled with a 1:15 THF/water mixture. The cold bath was set to reach $-10\text{ }^{\circ}\text{C}$ to ensure freezing occurred relatively fast. The freezing temperature of water is $0\text{ }^{\circ}\text{C}$, whereas

the formation temperature of a THF hydrate is ~ 4.4 °C. As shown in the figure, when the tubes containing water freeze, the temperature spikes to approximately 0 °C and remains constant for the duration of the freezing process. The temperature spikes to approximately 4 °C for the tubes containing THF and water. Therefore, it is reasonable to assume that THF hydrates are being formed instead of pure ice. Note that in all the experiments in this study, ice was not observed to form from a THF/water solution. It should be noted this method has also been used by Dai et al. to verify that a THF hydrate is formed instead of ice [94].

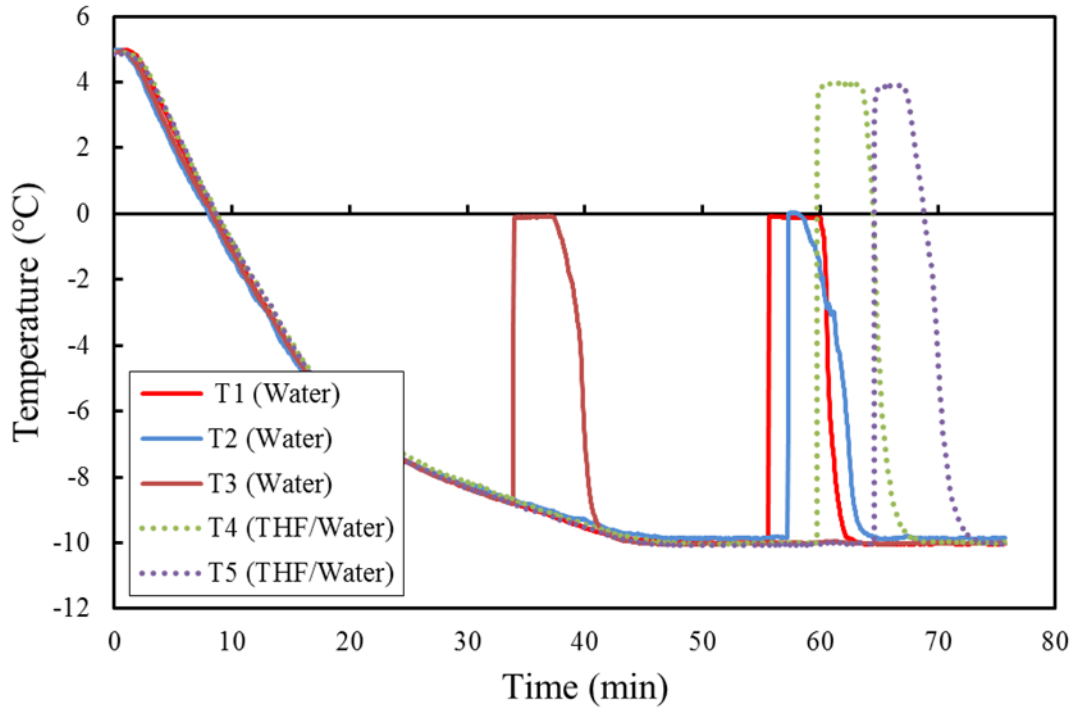


Figure 4.4. Comparison of the temperature vs. time history of water (T1, T2, and T3) and THF/water solutions (T4 and T5) in the cold bath.

4.2.2 Experimental procedure for the visualization of hydrate formation in droplets

THF evaporates rapidly, and the evaporation rate of THF-water solutions was determined before conducting the droplet-based experiments. A mass balance (Denver Instruments PI - 214, range of 0-210 g, resolution of 0.1 mg), was used to track the weight loss associated with evaporation of 0.24 mL of 1:15 THF/water solution. Figure 4.5 shows the mass loss with time and the percent mass loss with time.

From the above plot it is seen that less than a 5% mass loss occurs in 2 minutes. In the present visualization experiments, all droplets were observed to form hydrates

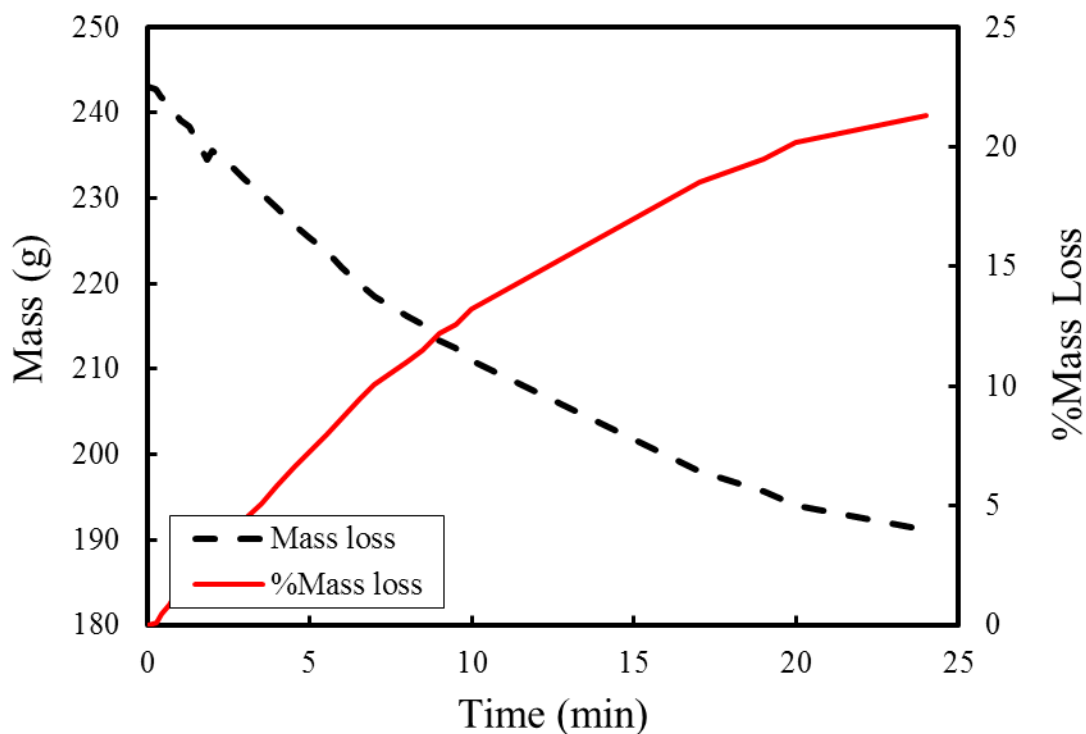


Figure 4.5. Mass loss and % mass loss vs. time due to evaporation from 0.24 mL of 1:15 THF/water solution.

in less than two minutes. It was therefore assumed that droplet mass loss during the experiment was insignificant.

To achieve THF hydrate formation in less than 2 minutes, the plate was set at 5 °C. After depositing a small pool of THF/water solution (~ 0.24 mL), the plate was set to cool at 10 °C/min. In all the experiments conducted with this setup, THF hydrates formed in less than 2 minutes.

4.3 Results

4.3.1 Effect of voltage and current on the formation of THF hydrates

Figure 4.6 shows the results of the experiments at 0, 10, 25, and 100 V with current as well as the 100-V/no-current experiments. It should be noted that all experiments were repeated at least twice (where each experiment consisted of 5 test tubes and 2 test tubes for the with-current and no-current experiments, respectively). Table 4.1 shows the number of total tubes tested for each voltage. Figure 4.6 shows the fraction of tubes that did not nucleate hydrates within a certain amount of time. For example, after 180 min, more than 95% of the tubes in the 0-V experiments had still not nucleated THF hydrates. In contrast, at 100 V with current, all the tubes nucleated THF hydrates within 10 min. Note that the 0-V experiments were allowed to run for as long as 15 hours. It is noted that even after 15 hours, 85% of the tubes had still not nucleated hydrates. The raw data for Figure 4.6 is included in Appendix B.

Figure 4.6 clearly shows that an electrofreezing voltage can substantially accelerate THF hydrate nucleation. As the voltage increases, the fraction of tubes that nucleate hydrates increases within any given time period. At high voltages (100 V), hydrates can be nucleated in less than 10 minutes. This is a significant advancement

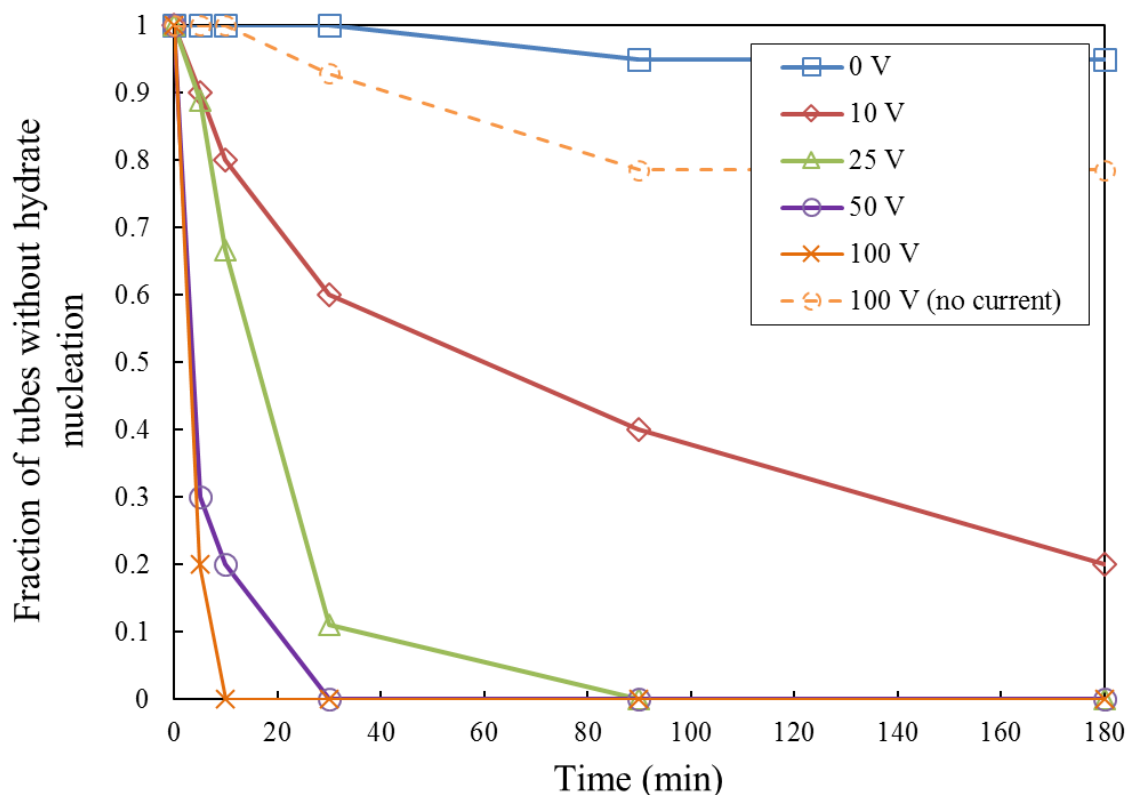


Figure 4.6. Fraction of tubes without hydrate nucleation vs. time. Experiments were conducted in a cold bath set at a temperature of $-5\text{ }^{\circ}\text{C}$. It is seen that electro-nucleation voltages can greatly accelerate hydrate formation. Note that 85% of the tubes in the 0-V experiments did not nucleate hydrates even after 15 hours.

in the field of hydrates, which can take hours and even days to nucleate.

Furthermore, the results of the 100-V/no-current experiments suggest that voltage alone is not responsible for inducing nucleation. The 100-V/no-current experiments had much fewer hydrate formation instances compared with the 100-V/current experiments. In fact, the 100-V/no-current experiments had fewer hydrate formation instances compared with even the 10-V/current experiments. It can be concluded that electric currents also affects the induction time. These results also agree with

Table 4.1. Number of experiments conducted to obtain the data for Figure 4.6. Note that 100* V denotes the experiment run at 100 V but without any current flow.

Voltage (V)	Number of experiments
0	20
10	10
25	9
50	10
100	10
100*	14

the results from Chapter 3, which showed that while an electric field alone can promote ice nucleation, the dual effect of electric fields and current flow is stronger at inducing nucleation.

In the above experiments, the measured current was the total current from all 5 tubes, which are in a parallel circuit. To further investigate the combined influence of voltage and current, single-tube experiments were conducted with the current being continuously recorded throughout the experiment. Figure 4.7 shows examples of the temperature vs. time curve and current vs. time curve at 25, 50, and 100 V (10 V was excluded from the test conditions since rapid nucleation was not observed at this voltage).

Several interesting features can be inferred from Figure 4.7. Firstly the current is seen to increase with voltage, as expected. At 25, 50, and 100 V, the pre-nucleation current was approximately 35, 110, and 250 μA . Note that the current fluctuates with time, and there is some variability across experiments, which can be attributed to bubbles growing and detaching from the electrodes (discussed later).

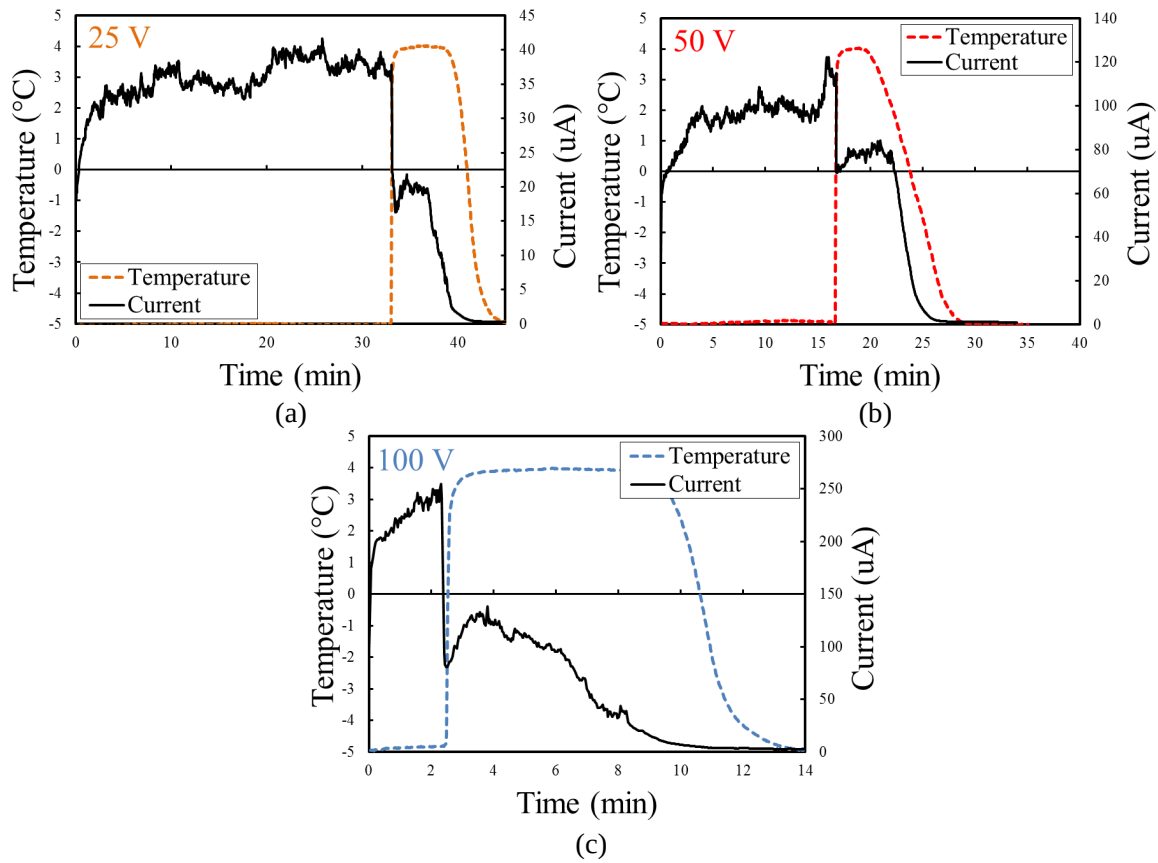


Figure 4.7. Temperature vs. time and current vs. time plots associated with formation of THF hydrates at a) 25 V, b) 50 V, and c) 100 V.

Secondly, hydrate nucleation is clearly accompanied by a sudden decrease in current flow. This suggests that hydrates first nucleate around the pinholes at the tip of the cathode, which blocks the current flow paths. As the hydrate crystal continues to grow, the current remains approximately constant before eventually decreasing to 0 by the time the hydrate forms within the entire tube. This observation is significant since it offers the possibility of inferring hydrate formation by tracking the thermal signature of the precursor solution. This technique has potential applications in monitoring hydrate formation in subsea pipelines and infrastructure.

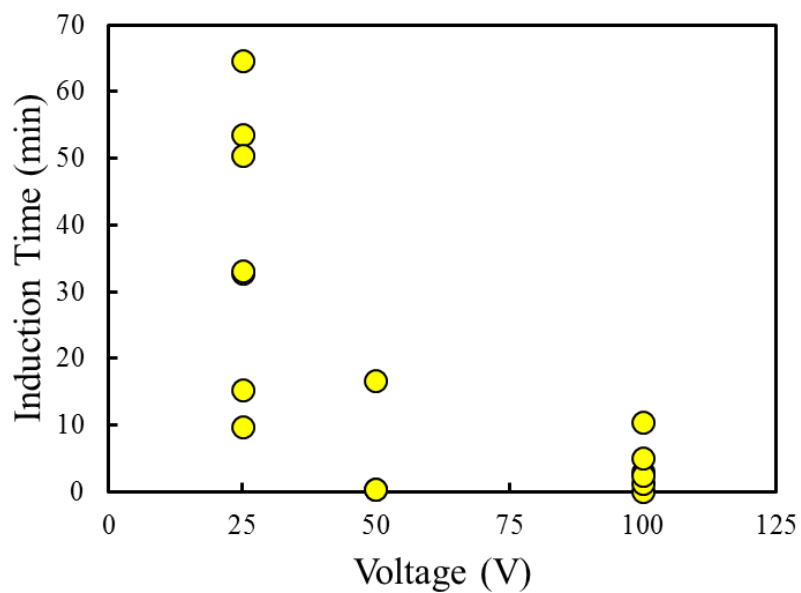
Thirdly, the effect of Joule heating appears to be negligible. Even at 100 V, the increase in temperature due to Joule heating is less than 0.2 °C, as shown in Figure 4.7(c), and clearly, does not hinder the rapid onset of nucleation.

In all, seven 25-V experiments, three 50-V experiments, and six 100-V experiments were conducted for a total of 16 single-tube experiments. Figure 4.8(a) shows the induction time versus voltage for the individual experiments, and Figure 4.8(b) shows the induction time versus current of the same individual experiments. Because the current fluctuates with time, the current plotted in Figure 4.8(b) is the current immediately recorded before nucleation, i.e., before the sudden decrease in current.

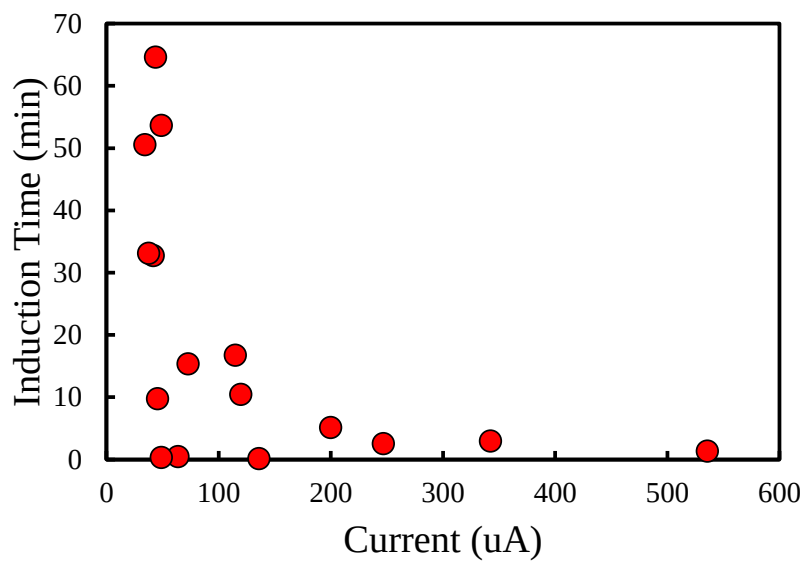
Figure 4.8(a) shows that at 25 V, the induction time is lowered considerably compared to the no voltage case. However, the spread in measured induction times is significant. In contrast, at 100 V, induction times are very low, and the spread in induction times is also reduced. Rapid hydrate nucleation has a much higher probability at 100 V compared to that at 25 V. Figure 4.8(b) suggests a very strong correlation between a high current and low induction time. The plot suggests that there is a threshold current requirement of approximately 150 μA to achieve an induction time of less than 10 minutes.

As seen in Figure 4.8, there were several instances where hydrate formation initiated instantaneously (less than a second) after applying a voltage. These results suggest that applying voltage pulses instead of a constant voltage could further lower the induction time. Overall, these results constitute a disruptive advancement in the field of hydrates, with ‘nucleation on demand’ opening the possibility of many novel applications involving hydrates

There are multiple explanations to explain rapid hydrate nucleation under electro-nucleation conditions. Firstly, as suggested in §3.4, the Gibbs free energy



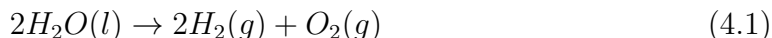
(a)



(b)

Figure 4.8. Measured induction times for THF hydrate nucleation in single-tube experiments. a) Induction time vs. voltage and b) Induction time vs. current.

required for activation is lowered with the application of an electric field; this aids nucleation. Secondly, bubble formation was observed on the electrodes (discussed later in this chapter), which suggests the possibility of electrolysis. The associated chemical reaction can be described by Eqn. 4.1, with hydrogen bubbles forming on the cathode and oxygen bubbles forming on the anode.



At standard pressure and temperature, the critical voltage required to initiate electrolysis is 1.23 V [146]; at lower temperatures, this critical voltage increases but not significantly (same order of magnitude) [147]. These bubbles create much more surface area and provide nucleation sites, which can significantly increase the likelihood of nucleation.

Thirdly, the gas bubbles are observed to flow in small streams. They can also grow and merge to form larger bubbles that eventually detach. The liquid convection and the pressure variations associated with bubble merging and detachment can impart the additional energy required to initiate hydrate nucleation from the supercooled precursor solution.

Separate visualization experiments were conducted to obtain qualitative comparisons of bubble formation at various voltages. Figure 4.9 shows the difference in the size and distribution of bubbles on the cathode at 10, 50, and 100 V. These images were taken with the high-speed camera under room temperature conditions. No hydrate nucleation was expected under such conditions. However, it is clearly seen that bubble formation occurs on the cathode. Furthermore, the number and size of bubbles is greater at 100 V than at 10 V. Also, the rate of bubble growth is greater at higher voltages, and the small streams of bubbles have a greater velocity as the

voltage increases. For example, at 100 V, the velocity of streams of tiny bubbles (size <0.05 mm) was approximately 1 mm/s, which is much larger than those at 50 V (0.4 mm/s) and 10 V (0.2 mm/s). In addition to the streams of tiny bubbles, the detachment velocities of the larger bubbles (diameter ~ 0.5 mm) at 100 V and 50 V were approximately 20 mm/s and 10 mm/s, respectively. At 10 V, no detachment of bubbles was observed. It is important to note that the convection effects related to bubble departure can be quantified by these measurements.

While the present experiments do not definitively reveal the dominant factor underlying rapid nucleation, they do indicate that current flow and the associated bubble formation due to electrode reactions is the most likely mechanism. Future

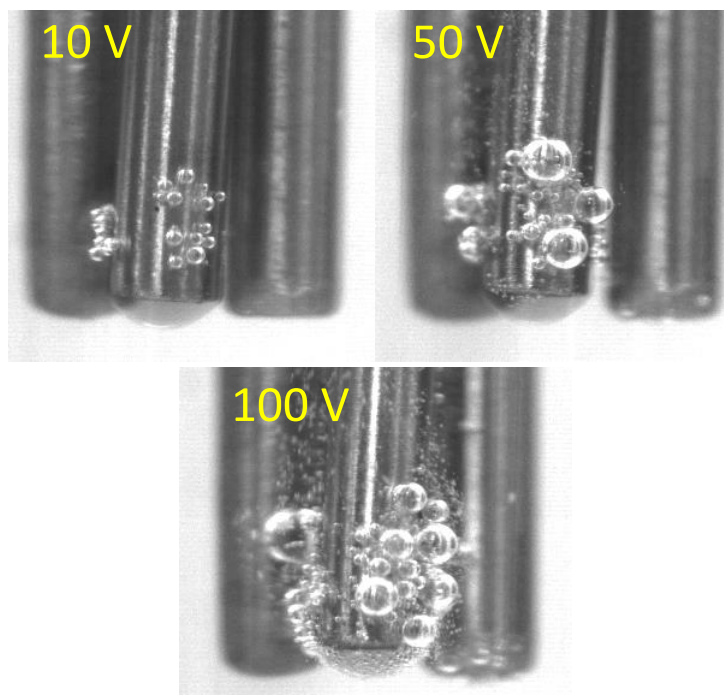


Figure 4.9. Illustrations of bubble formation on the cathode during electro-nucleation experiments with THF/water solutions at 10, 50, and 100 V. Note that all of these images were taken 1 min after turning on the voltage.

experiments can explore the influence of geometry and spacing of the pinholes on bubble size, bubble growth rate, bubble velocities, and relate it to the measured induction times.

4.3.2 Visualization of THF hydrate formation in droplets

The previously described experiments were performed in a cold bath, which eliminated visualization of the hydrate nucleation process. Therefore, visualization experiments were conducted with drops using the setup and procedure described in §4.2.2.

Large drops of THF-water solutions (0.24 mL) were used in these experiments to minimize any effects due to evaporation. Experiments were conducted with the cold plate temperature ramping down at 10 °C/min. Nucleation of THF hydrate formation was visualized from the top and is shown in Figure 4.10.

Similar to ice nucleation, a two-stage formation of THF hydrates was observed. As described in §2.2.2, in the first stage of formation, nucleation starts at a point on the three-phase contact line, and a “formation front” rapidly sweeps across the fluid volume. This first stage is of very short duration compared with the second stage. In the second stage, the liquid mass fully forms and solidifies. This process begins at the base of the drop, and the solidification front moves upwards, where the tip of the drop is the last to solidify.

Figure 4.10 shows the two-stage formation process for THF hydrates. Nucleation begins at the three-phase contact line and sweeps across the drop during the first stage. After the first stage is complete, the second stage begins, where solidification begins at the base of the drop and moves upwards. It should be noted that no voltages were applied in the experiment described in Figure 4.10.

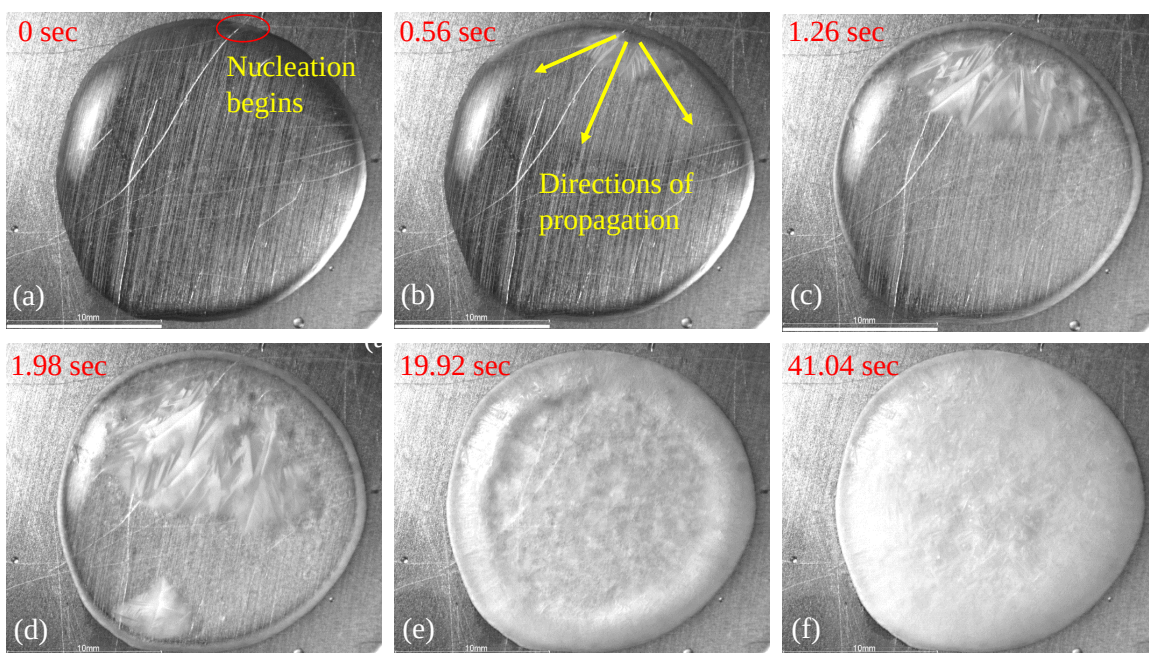


Figure 4.10. Two freezing stages are involved in the formation of THF hydrates from 1:15 THF:water solution. The first stage of formation is depicted in the top row, where nucleation initiates at the three-phase line. The second row shows the second stage of formation, where the drop solidifies from the base of the drop to the top.

Figure 4.11 shows images at the beginning of the first stage of THF formation under 100 V and 0 V. As described in §4.2.2, a 0.5-mil polyimide layer was used as the dielectric layer, with a single pinhole created in the layer to allow current flow. Figure 4.11 shows that nucleation tends to initiate at the site of the pinhole in the dielectric layer regardless of the presence or absence of voltage. This is interesting since the most common location for nucleation initiation is the three-phase line (as shown in the middle image of the bottom row. Note that there was an instance of nucleation at the three-phase line). One explanation for nucleation initiation at the pinhole site is the presence of bubbles, which act as potential nucleation sites. However, this argument cannot be completely validated using the present experiments since the

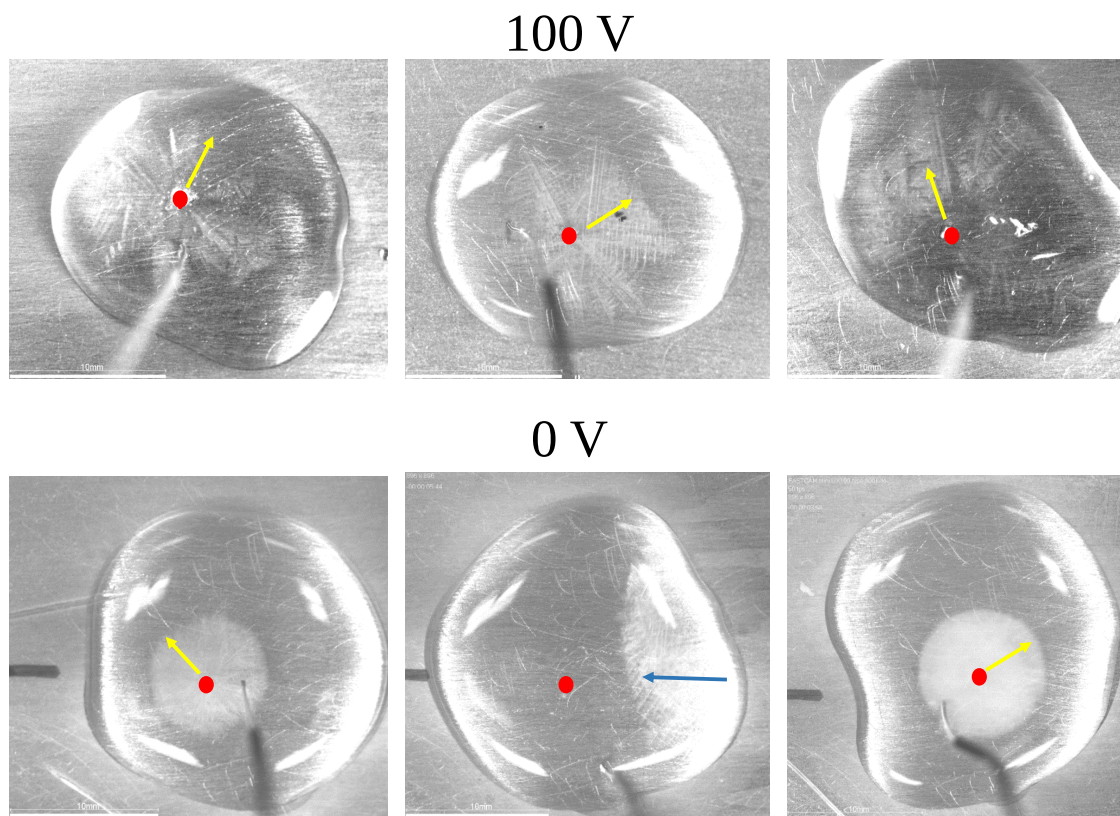


Figure 4.11. Images depicting the first stage during formation of THF hydrates under electro-nucleation conditions. 100 V was applied in the experiment shown in the top row, and no voltage was applied in the experiment shown on the bottom row. The red dot indicates the location of the single pinhole in the dielectric layer, and the arrows indicate the direction of propagation of the formation front.

nucleation site was unchanged in the absence of voltages (and bubbles). Another explanation for the location of the nucleation site being the pinhole is the fact that it is the coldest point in the dielectric layer. Overall, these experiments suggest that pinhole related effects (current flow, bubbles, convection) offer a strong explanation for rapid nucleation; however the present experiments cannot be considered to be completely conclusive in nature.

One interesting observation from the images in Figure 4.11 is the difference in crystal morphology between the 100 V and 0 V experiments. At 100 V, the crystals appear more dendrite-like, whereas at 0 V, large dendrites are not observable. This suggests that smaller crystals form during the first stage of formation in the absence of voltages.

While the present work successfully showed a reduction in the nucleation induction time of THF hydrates, this work can be extended to address other challenges. These include increasing the hydrate front propagation rate and ensuring that ice is not formed, i.e., ensuring a high water-to-hydrate conversion ratio.

4.4 Conclusions

This chapter presented a novel technique to achieve rapid hydrate nucleation via electro-nucleation; this approach eliminates the use of stirrers or chemical promoters. Experiments were conducted to electro-nucleate THF hydrates in a constant-temperature bath, and the induction time was measured by tracking the thermal signature of the precursor solution. The effect of voltage and current on hydrate nucleation was explored by accommodating current pathways (via pinholes) in a typical electrowetting setup.

In the absence of electrofreezing voltages, THF hydrates can take tens of hours to nucleate. Low voltages (10 V) can promote nucleation within 3 hours. At high voltages, very rapid nucleation can be observed (<10 minutes). Parametric experiments reveal that the electric current flow is responsible for accelerated nucleation; the use of high voltages without current flow did not lead to rapid nucleation. Current flow is accompanied by chemical reactions and bubbling at the interface. The availability of additional nucleation sites (bubbles) and bubble-related phenomena (growth,

oscillations, convection, and detachment) can also act as triggers for nucleation.

These results indicate that voltage-induced currents are essential to rapidly form hydrates. The results also suggest that there is a voltage/current threshold, above which, rapid hydrate formation will occur. It is expected that these results can be extended to other hydrate systems, such as methane hydrates (which have a similar structure as THF hydrates), which are being studied for a variety of energy-related applications.

Chapter 5

Conclusions and suggestions for future work

This chapter summarizes the key findings emerging out of this dissertation and outlines future research directions in the field of nucleation/formation of ice and hydrates.

5.1 Major scientific findings and contributions of this dissertation

This dissertation has resulted in valuable scientific contributions to the field of ice and hydrate formation. The major scientific advancements emerging from this work are summarized ahead.

5.1.1 Comparison of saltwater and freshwater ice nucleation (Objective 1)

The majority of studies on icephobicity assess freshwater icing despite an abundance of applications that involve saltwater (marine icing). Fundamental studies were conducted to explore the differences between freshwater and saltwater icing. The major scientific conclusions from this study include:

- It is seen that surface chemistry alone does not significantly affect the freezing temperature of static freshwater or saltwater droplets.
- Saltwater droplet impact dynamics on superhydrophobic surfaces are different

from pure water. Saltwater droplets retract more and a greater fraction of impacting liquid is repelled from the surface.

- The greater bounciness of saltwater droplets is a result of slower ice nucleation propagation kinetics.
- This study suggests that superhydrophobic surfaces will offer greater resistance to impact icing with saltwater than pure water and can remain useful at temperatures as low as $-40\text{ }^{\circ}\text{C}$ (for saltwater applications).

Overall, this work is a starting point for further studies on heterogeneous saltwater nucleation and serves as a bridge between freshwater icephobic surfaces and saltwater applications.

5.1.2 Electrofreezing-based elevation of freezing temperatures (Objective 2)

Despite the abundance of studies on electrofreezing, the basic mechanisms underlying electrofreezing were not clear. Fundamental studies were conducted to isolate the influence of electric fields and electric current on ice nucleation. The major scientific conclusions from this study include:

- Electric fields alone can elevate freezing temperatures by more than $15\text{ }^{\circ}\text{C}$ in the absence of current flow.
- Electrofreezing induced temperature elevation saturates at high electric field strengths.
- Polarity of the interfacial charge does not significantly influence electrofreezing.

- Electric currents can further elevate the freezing temperatures by providing nucleation sites (via bubble formation) and other triggers for nucleation.

Overall, it is seen that the electric field and the electric current both influence electrofreezing; however, the physical mechanisms are very different.

5.1.3 Rapid nucleation of hydrates by electro-nucleation (Objective 3)

The large nucleation times (ranging from hours to days) for hydrate formation are a significant problem for many hydrate-based systems. This study develops and characterizes electro-nucleation as a new technique for controlling and inducing rapid hydrate formation. The major scientific conclusions from this study include:

- Hydrate nucleation can be achieved in less than ten minutes with the use of electro-nucleation fields.
- This study quantifies the relations between the applied voltage/current and the induction time. Higher voltages reduce the induction time in a non-linear fashion.
- Voltage-induced current flow appears to be responsible for rapid nucleation. Current flow is accompanied by chemical reactions and bubble formation at the surface, which provides triggers for rapid nucleation.
- Hydrate formation under an electro-nucleation electric field is accompanied by a sudden decrease in the current at the onset of nucleation. This finding can be the basis for the detection of hydrate formation in many industrial applications.

Overall, this study lays the foundation for a new tool to promote hydrate formation (in addition to mechanical stirring and addition of chemical additives).

5.2 Recommendations for future work

The results of the present studies lay the foundation for future research on the topic of electrofreezing with applications in the areas of ice and hydrates. Three potential lines of enquiry are described ahead.

5.2.1 Understanding the role of current flow and relevant phenomena on electrofreezing

The present work clearly shows that current flow is essential to enhance the nucleation of ice and hydrates. However, the exact mechanism responsible for nucleation promotion is not yet clear. Carefully planned experiments can be conducted to isolate and quantify the effects of the phenomena that occur when current flows between electrodes. Variables, such as the number, size, distribution, velocity, and growth rate of the bubbles, can be controlled, and their effect should be systematically investigated. Such measurements can also enable a better understanding of heat transfer mechanisms near the surface. Additionally, the effect of different electrode materials should be investigated since multiple studies have hinted at electrofreezing-dependence on electrode material [60, 115]. Importantly, the effect of voltage/current *pulses* on the induction time should be investigated; this is based on very exciting preliminary results that show ‘instantaneous nucleation’ upon the application of a voltage (Figure 4.8). The ultimate objective of all these experiments is to identify the electro-nucleation conditions that minimize the induction time while minimizing the required voltage and current.

As a follow up of the present work, an interesting line of study could focus on isolating the role of electromagnetic phenomena (compared to mechanical phenomena) on inducing rapid nucleation. As an illustration, an experiment that uses a different way to form bubbles (without moving parts and without using electric fields) can

pinpoint the influence of bubbles on nucleation.

5.2.2 Electrofreezing of complex fluids and solutions

The results of Chapters 3 and 4 suggest that electrofreezing can work with other fluids. Electrofreezing as a tool to control saltwater icing is an intriguing prospect. The influence of ions in water can be investigated, and experiments can be conducted with multiple ions (to simulate seawater more accurately). All such experiments with more complex fluids would further enhance our understanding of electrofreezing.

5.2.3 Electro-nucleation of other hydrates

While the present work focused on rapid electro-nucleation of THF hydrates, a logical extension is the study of electro-nucleation for other types of hydrates.

The next logical step would be to conduct similar experiments to form cyclopentane hydrates. Cyclopentane forms hydrates at atmospheric pressure, however, it is immiscible with water (unlike THF). It is possible that the location at which current flow originates on the electrode is an important variable that affects hydrate formation; this could be assessed via experiments with cyclopentane hydrates. Ultimately, the greatest value of this work will be for the rapid formation of methane hydrates since it has a large number of applications. Conducting electrical experiments in pressurized vessels used for methane hydrate formation is challenging. However, there is potential for the development of game-changing energy technology.

It should also be noted that bubble formation and growth could be suppressed at the high pressures required for methane hydrate formation. This indicates that higher voltages might be required for such systems; furthermore the solubility of the

gas in the bubbles at high pressure becomes an important parameter. All of these high-pressure relevant phenomena highlight the importance of well-planned and well instrumented experiments to study electro-nucleation of methane hydrates.

5.2.4 Influence of electro-nucleation on the growth rate and conversion ratio of gas to solid hydrates

In addition to reducing the induction time, high growth rates and high gas-to-hydrate conversions ratios are needed for viable hydrate-based technology. The freezing visualizations of THF hydrates in Chapter 4 suggest that the crystal morphology changes when a voltage is applied, which would likely affect the conversion ratio. Also, the growth rate of hydrates are limited by their release of latent heat during formation. Joule heating from the electro-nucleation technique could negatively affect the growth rate. Both of these variables should be investigated.

An exciting prospect to increase both the growth rate and the ratio of gas to hydrate conversion ratios is the use of high-porosity metal foam. Very little work has been reported on the use of metal foam and gas hydrate formation, as described in §1.2.3. Yang et al. experimentally investigated the effect of aluminum foam (average pore size of 1000 μm) on the formation and growth kinetics of methane hydrates with SDS but without stirring [113]. The results demonstrated that the aluminum foam not only accelerated the induction time but also increased the rate of formation and growth. It is believed that metal foam enhances the methane-water contacts and due to the foam's large surface area and excellent thermal conductivity, can more effectively remove the heat released during hydrate formation.

First, due to the lack of studies on the subject, additional studies are needed to investigate the use of metal foam to accelerate hydrate formation. Second, the electrofreezing technique could easily be adapted to a setup with metal foam, where

the metal foam could be used as the ground electrode. The combined effect of electro-nucleation and the metal foam to remove heat and increase gas-water contacts could address all three major limitations of current hydrate-based technology by reducing the induction time, accelerating hydrate growth, and increasing the gas-to-hydrate conversion ratio.

Appendices

Appendix A

Surface temperature calculations

The results in Chapters 2 and 3 are presented in terms of the temperature at the interface of the droplet and the substrate. However, the infrared camera cannot directly measure the surface temperature but instead measures the temperature of the top of the droplet. The interface temperature (T_{surface}) was estimated using a steady state, 1-D heat transfer analysis.

This appendix first outlines the analysis to estimate the interface temperature for the static saltwater droplet freezing experiments (Chapter 2) and the electrofreezing experiments (Chapter 3). Subsequently, the analysis to estimate the interface temperature during the droplet impact experiments (Chapter 2) is described.

A.1 Analyses for the static saltwater droplet freezing experiments (Chapter 2) and the electrofreezing experiments (Chapter 3)

Figure A.1 shows the cross-section of the devices used in the electrofreezing and the static saltwater droplet freezing experiments. Under steady state, 1-D heat transfer assumptions, the heat flux is constant through the water droplet and all the other layers between the droplet and the cold plate, which can be captured by the following equation:

$$\frac{T_{\text{drop}} - T_{\text{plate}}}{R_{\text{total}}} = \frac{T_{\text{drop}} - T_{\text{surface}}}{R_{\text{water}}} \quad (\text{A.1})$$

where T_{drop} is the droplet temperature measured with the infrared camera, T_{plate} is the plate temperature, which is measured using a $100\ \Omega$ platinum RTD with a resolution of $0.01\ ^\circ\text{C}$ within the plate, T_{surface} is the surface temperature, and R is the thermal resistance, which is defined as the following:

$$\frac{L}{kA} \quad (\text{A.2})$$

where L is the thickness, k is the thermal conductivity, and A is the cross-section area. R_{total} is the sum of all the thermal resistances.

With a knowledge of the thermal conductivities, thicknesses, and the droplet

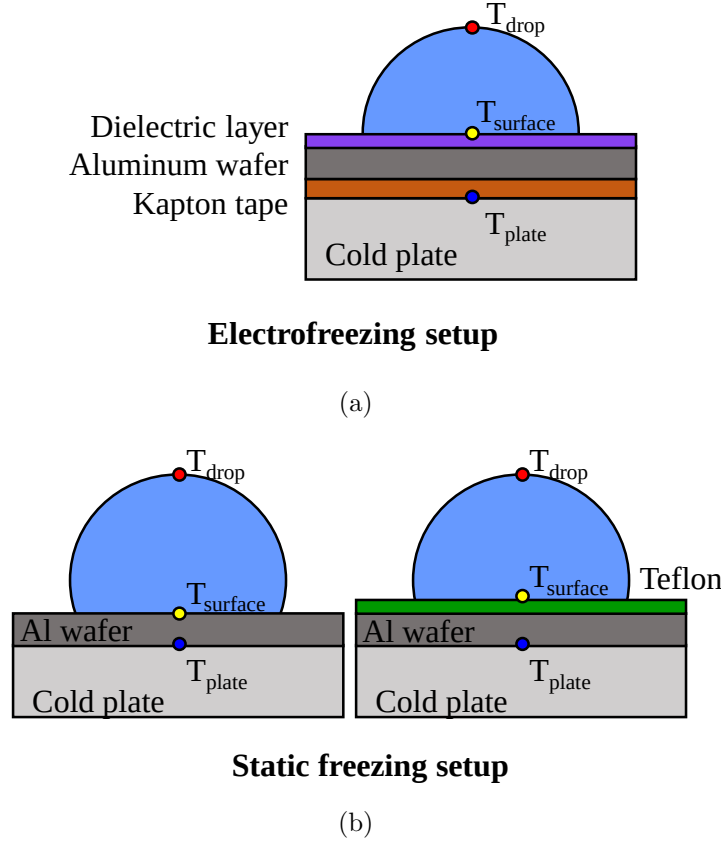


Figure A.1. Schematic showing various temperatures of interest in the electrofreezing and static saltwater droplet freezing experiments.

and plate temperatures, the surface temperature of the droplet can be estimated. A thermal conductivity of 0.12 W/mK was used for the polyimide film (Kapton tape), Teflon, and CYTOP. The thermal conductivities of water and the aluminum wafer are 0.58 and 167 W/mK, respectively.

In Eqn. A.1, T_{drop} is measured directly by the IR camera, and T_{plate} is measured by the RTD in the plate. Before solving for T_{surface} , the linear relationship between T_{drop} and T_{plate} must be known, i.e., $T_{\text{plate}} = A * T_{\text{drop}} + B$. Then, T_{surface} in Eqn. A.1 can be determined given the T_{drop} measurement and the calculated thermal resistances. The relationship between the droplet temperature and plate temperature for each configuration was obtained by a short series of experiments. The previously described experimental procedure was employed, i.e., droplet deposition followed by cooling at 5 °C/min. The plate temperature and the droplet temperatures were recorded at the instant that the plate temperature reached 10, 0, -10, -15, -20, and -25 °C. A linear relation between the average droplet temperatures and the plate temperature was obtained. This procedure was repeated three times for each configuration to obtain the final linear relation used to estimate the surface temperature from the recorded droplet temperatures.

A.2 Analyses for the droplet impact freezing experiments (Chapter 2)

A similar analysis as above was employed to determine the surface temperature of the Teflon-coated roughened copper plate. However, unlike the previous smooth surfaces, the droplet on a superhydrophobic surface rests on a composite interface of part air and part solid. As will be shown below, the insulating effect of the air gaps is insignificant due to the high thermal conductivity of copper.

Instead of recording the temperature at the top of a water droplet, black electrical tape (known emissivity) was attached to the surface. Experiments were conducted at plate temperatures of 20, 0, -15, -30, and -40 °C. The procedure consisted of ramping down to the desired plate temperature, holding a steady temperature for 5 minutes, and then recording the temperature at multiple locations on the electrical tape. Thus, a linear relationship was obtained between the tape temperature and the plate temperature.

This relationship can be used to estimate the surface temperature using a thermal resistance calculation. Unlike the experiments with smooth surfaces, the resistances of the copper peaks and air gaps are in parallel. It is noted that the Teflon layer can be ignored because it is very low thickness ($<1 \mu\text{m}$).

The water meniscus is partly supported on the copper structures and partly contacts the air pockets. The resistances of the copper structures and air gaps can be considered to be in parallel. For such a resistance network, the effective thermal resistance will be governed by the smaller of the two resistances. The effective thermal resistance R_{eff} can be expressed as

$$R_{\text{eff}} = \frac{R_{\text{air}} R_{\text{Cu peaks}}}{(R_{\text{air}} + R_{\text{Cu peaks}})} \quad (\text{A.3})$$

If $R_{\text{air}} \gg R_{\text{Cu peaks}}$, then $R_{\text{eff}} \sim R_{\text{Cu peaks}}$

Because the thermal conductivity of copper is more than 13,000 times that of air, the thermal resistance of the copper pathway is much less than that of air. Even if the fraction of the water meniscus area in contact with air is 0.95 (i.e., a very high value), the effective thermal resistance will still be close to the thermal resistance of copper as per the above equation. Essentially, all the heat flow through the layer

occurs via the copper pathways. The role of air pockets would be important if the substrate had a lower thermal conductivity comparable to that of air.

Appendix B

Raw data of experimental results presented in Figure 4.6

Table B.1 contains the raw data that were used to create Figure 4.6. Note that the numbers 1-5 indicate the 5 electrode sets (consisting of the anode, cathode, and thermocouple), i.e., all of the induction times in column 1 were from the same electrode set. 100* indicates the 100 V/no-current experiment. The *Total Test Time* refers to the amount of time the experiment was allowed to run. The ‘-’ indicates that nucleation was not observed during the test. The ‘x’ indicates that the particular electrode set was not used during the experiment.

Table B.1. Raw data presented in Figure 4.6.

Induction time (min)						Total Test
Voltage	1	2	3	4	5	Time
0	-	-	-	-	-	16 hrs
0	62.1	306.1	-	-	-	15 hrs
0	-	-	-	-	-	15 hrs
0	-	-	763.1	-	-	17 hrs
10	-	29.4	64.8	19.1	118.5	3 hrs
10	38.7	95.4	-	7.2	3.4	3 hrs
25	19.6	7.1	8.9	3.8	16.5	-
25	14	14.8	-2.7	48.1	13.6	-
50	1.8	1.7	10.3	17.1	1.4	-
50	5.9	4.7	1.5	4.5	0.8	-
100	5.6	3.1	4.5	2.9	0.2	-
100	1.8	3.3	2.3	6.9	3.9	-
100*	x	24	-	x	x	3 hrs
100*	x	-	-	x	x	3 hrs
100*	x	-	-	x	x	3 hrs
100*	x	33.8	-	x	x	3 hrs
100*	x	-	72.6	x	x	11 hrs
100*	x	-	-	x	x	4 hrs
100*	x	-	-	x	x	4 hrs

Appendix C

High-pressure methane hydrate cell

The primary objective of the effort on methane hydrate formation was to gain familiarity with the processes involved in forming methane hydrates. Successful synthesis of methane hydrates is the starting point for future electro-nucleation experiments with methane hydrates. This work is on-going and will continue beyond this dissertation.

Methane forms a structure I hydrate; this structure contains 46 water molecules that surround 2 small cavities and 6 medium-sized cavities, as shown in Figure 1.8 in §1.2.3. The chemical formula for a methane hydrate is XCH_446H_2O , where X is typically less than 8 [90]. Figure C.1 shows the methane hydrate stability curve, which also shows how the hydrate-gas phase boundary shifts in the presence of other entities when other compounds are present, such as NaCl and CO_2 .

An experimental setup was previously developed in the Petroleum and Geosystems Engineering Department at The University of Texas at Austin by Divya Ramaswamy, a Masters student of Professor Mukul Sharma. This setup is currently being reconfigured to form methane hydrates. The experimental setup and the experimental procedure is briefly described ahead.

As shown in the schematic of Figure C.2, the methane hydrate setup consists of a stainless steel high-pressure hydrate cell, cold bath, methane gas accumulator, pump, insulated cooler, data logger, and a PC. The internal length and inner diameter

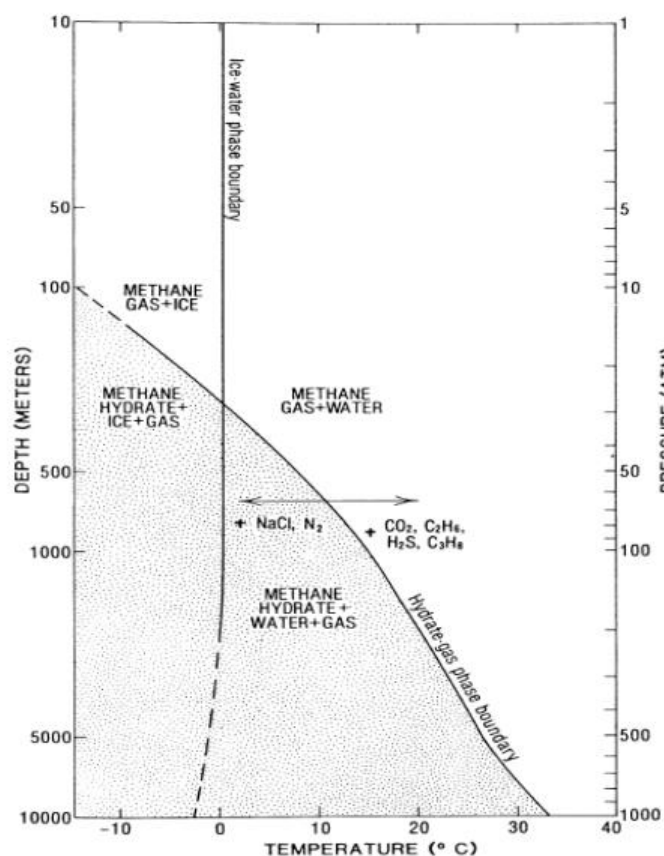


Figure C.1. Methane hydrate stability curve. Reprinted with permission from [24].

of the hydrate cell is 15 cm and 1.785 cm, respectively (volume of 42.25 cm³). Figure C.3 shows images of the hydrate cell. Both methane and water are delivered to the cell via valves, as shown in the figure. The hydrate cell is completely immersed in water in the cooler; this water is cooled by pumping refrigerant (from the cold bath) through a coiled copper tubing immersed in the cooler. The thermocouple is connected to a DAQ, which is connected to a PC; a LABVIEW program is used to monitor and record the temperature within the hydrate cell measured by the thermocouple (Type T).

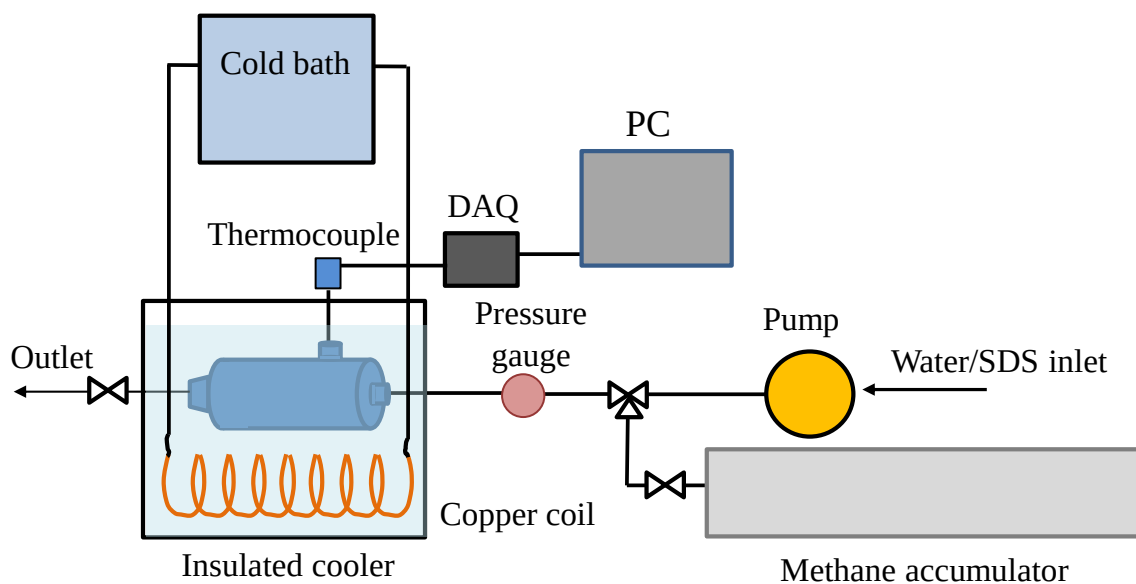


Figure C.2. Schematic of the experimental setup to form methane hydrates.



Figure C.3. Images of the high-pressure methane hydrate cell.

A surfactant, sodium dodecyl sulfate (SDS), was mixed with deionized water and fed into the hydrate cell (0.3 g/100 mL was used). SDS is used to reduce the induction time of hydrate formation.

The following is the basic procedure that will be employed to form methane hydrates:

1. The high-pressure cell and tubing are cleaned by flowing water through the entire setup for approximately 10 minutes. During this time, the setup is also checked for leaks.
2. Any trapped air is expelled from the cell by purging with methane.
3. The pipes are purged with the water/SDS solution.
4. The bath temperature is set to 2.5 °C.
5. Methane gas is pumped until a pressure of 826 psi is reached.
6. Water is then pumped into the cell until a final pressure of 1200 psi is reached.
7. The LABVIEW program begins recording.
8. The sample is left undisturbed until a hydrate forms, which is signaled by a sudden drop in pressure and temperature.

As mentioned in the early part of the introduction, this work is on-going and will continue in the post-dissertation period.

Appendix D

Additional work conducted during Ph.D. tenure

In addition to the work reported in this dissertation, another research project was successfully conducted over the course of the Ph.D. program. Below is an abstract of an article published in International Journal of Heat and Mass Transfer (with Prof. Alexandre da Silva as the Ph.D. advisor) [148].

Abstract

In this study, aluminum foam test sections with discrete pore-size gradients were experimentally investigated. The test sections, which were created by combining foams with up to three different values of pores per inch (PPI), were uniformly heated from below by a flat heater and cooled by a controlled air stream flowing through the foam. The overall dimensions of the foams tested were 25.4 mm wide and 6.4 mm thick, and the individual length of a foam section varied between 101.6 mm, 50.8 mm, and 25.4 mm, depending on the number of segments with different PPIs being tested. The pressure drops were measured, and the heat transfer coefficients were calculated for all foam combinations considered. The hydrodynamic results showed that the number of sections did not affect the overall pressure drop across the test section if all segments had the same PPI. Also, a higher heat transfer coefficient was observed when air flowed first through the foam with the larger pores (smaller PPI) compared with that of the test section in the reversed orientation. However, the heat transfer coefficients of the mixed-foam test sections were not greater than their better performing whole-foam counterpart, at least for the samples tested. This suggests

that, perhaps, metal foams with more refined geometric features could be exploited to allow the tradeoffs between heat transfer, required pumping power, weight, etc., to become identifiable.

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