Investigation of the Effects of Surfactant Concentration on the Boiling Curve of Water

by

Darci Janelle Reed

Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Bachelor of Science in Mechanical Engineering at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Abstract

Boiling is a widely used heat transfer process in industry that allows for high heat transfer with a small temperature gradient. In this study the effects of two homologous series of surfactants (trimethylammonium bromide (TAB) and methylglucamine (MEGA)) on the boiling curve of water were explored. Heat transfer vs. temperature plots were obtained for five surfactants for various concentrations under the critical micelle concentration (CMC). Plots of temperature vs concentration for specific heat fluxes showed the lowering of the superheat that improves heat transfer when surfactants were added, resulting in an overall left shift of the boiling curve. The shifting that occurs at low concentrations of surfactant seem correlated with the diffusion coefficients of the different surfactants. The large shifting that occurs at larger concentrations is correlated with the hydrophobic tail length of each of the surfactants. This supports the hypothesis that the lowering of the dynamic surface tension, which correlates with the diffusion coefficient, is responsible for part of the lowering of the superheat. The fact that the larger shifting is correlated with the hydrophobic tail length supports the hypothesis that part of the shifting occurs due to the surfactants adsorbing onto the surface, making it more hydrophobic, increasing the contact angle, and decreasing the nucleation energy. The results of this work add to the understanding of the effects surfactants have on the boiling of water and give engineers more tools to adjust heat.

Thesis Supervisor: Evelyn N Wang
Title: Associate Professor
Acknowledgments

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Chapter 1

Background

Boiling is used in many different industries as a heat transfer mechanism. It is incredibly efficient because it uses the latent heat to achieve a high heat flux for a relatively low temperature difference, and is widely used in chemical processing, electronics cooling, and power production. In 2009, the US produced 520,000 terrajoules of steam. In 2005, it was estimated that roughly half of all American industrial energy use goes towards steam production for industrial processes. [4]

Improvements in boiling would help the precision and speed of these processes, and would also greatly increase their efficiency. Developments in boiling analysis would make a big difference in one of the nation’s largest industrial processes. This study analyses boiling and explores the use of surfactants to enhance boiling heat transfer.

1.1 Surfactants

1.1.1 General Introduction

A surfactant is a chemical that tends to reduce the surface tension of water. They have unique properties due to their amphiphilic structure. This means that they have a hydrophilic polar group attached to a hydrophobic group, which is often a carbon chain. [7] This unique structure means that it dissolves in water, but will aggregate
at interfaces and reduce the surface tension.

Previous work has shown that the addition of surfactants to water greatly enhances heat transfer. It appears to be related to the change in surface tension and the change in contact angle with the boiling surface brought about by the surfactant. It has been found that there is an optimum point, after which the addition of more surfactant no longer enhances heat transfer. This maximum enhancement point seems to be close to the critical micelle concentration for the surfactant. [7]

### 1.1.2 Water Properties

In surfactant solutions, the critical micelle concentration (CMC) is the concentration at which the molecules of the surfactant transition from a monomeric distribution to aggregation into micelles. For boiling enhancement, only concentrations at or below the CMC for each surfactant were considered. The CMC concentration is generally very low, on the order of a few mM, so at the considered concentrations most of the bulk properties, including viscosity, thermal conductivity, specific heat, and saturation temperature are approximately unchanged [7]. There is one property that is significantly changed: surface tension. The surface tension experiences changes even at very low concentrations due to the fact that the molecules tend to adsorb at interfaces. This surface tension varies with time in new bubble because the surfactants do not adsorb until an interface exists. Due to the low concentrations used in this study, it is assumed that all properties but surface tension remain the same throughout.

### 1.1.3 Materials Summary

A total of five different surfactants were tested in this study comprising two homologous series: trimethylammonium bromide (TAB) and methylglucamine (MEGA). Three different carbon tail lengths of TAB (10, 12, and 14 carbons long) and two different carbon tail lengths of MEGA were tested (8 and 10 carbons long). Table 1.1 shows the basic properties of each of these surfactants along with the chemical name of each surfactant, and the name each will be referred to in this paper.
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<tr>
<td>MEGA-8</td>
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</tr>
</tbody>
</table>

Table 1.1: This table gives the basic properties of the surfactants tested in this study.

### 1.1.4 Dynamic Surface Tension

The formation of a bubble creates a new liquid-vapor interface that the surfactant molecules diffuse on to. The concentration of surfactant at the interface, and thus the surface tension at the interface, is time dependent, but the bubble only has a lifetime of less than approximately 50 ms before it departs, so these changes are generally small.

Solving the 1-D diffusion equation \( \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \) for monomer concentration, using conservation of mass and assuming that the subsurface concentration is zero gives an equation for the concentration at the interface:

\[
\Gamma_{lv} = 2C_{1,\text{Bulk}} \sqrt{\frac{D_1 t}{\pi}}
\]

where \( \Gamma_{lv} \) is the monomer surface concentration, \( C_{1,\text{Bulk}} \) is the bulk concentration of the water, \( D_1 \) is the diffusivity of the surfactant, and \( t \) is time from the creation of the interface. Combining an ideal gas type surface equation with equation 1.1 results in an equation for the dynamic surface tension of water:

\[
\gamma_{lv} = \gamma_{lv,0} - 2RT\Gamma_{lv}
\]

\( \gamma_{lv} \) is the surface tension at any given time, \( \gamma_{lv,0} \) is the surface tension of water, \( R \) is the ideal gas constant, and \( T \) is the temperature. These equations show that the main variables controlling surface tension are the concentration of the surfactant and the diffusion coefficient of the surfactant.

For this study, we do not generally know the exact diffusion coefficients, so the surface tension at any point in time cannot actually be calculated. However, this
allows us to see the general trend. Increasing concentration decreases the surface tension, and since the diffusivity is generally higher with smaller molecules, the surfactants with lower molecular weight should generally have a stronger effect on the surface tension.

### 1.1.5 Approximate Diffusion Coefficient

While the exact diffusion coefficient of these surfactants has not been measured, it can be estimated. With the assumption that the diffusion coefficient is limited by a sphere with the cross section the size of the large polar head, the Stokes-Einstein equation can be used [5]:

\[
D = \frac{k_B T}{6 \pi \eta r}
\]

where \(D\) is the diffusivity, \(k_B\) is Boltzmann’s constant, \(T\) is the temperature, \(\eta\) is the dynamic viscosity of the fluid, and \(r\) is the radius of the spherical particle. The cross sectional area of the TAB head-group is 23 Å² [2] and the MEGA group is 62 Å² [1]. This give diffusion coefficients of \(9.62 \times 10^{-6}\) cm² s⁻¹ and \(6.91 \times 10^{-6}\) cm² s⁻¹ respectively. The diffusion of the TAB group is about 40% faster than that of the MEGA group.

This gives an idea of what to look for when the change in boiling is heavily dependent on the dynamic surface tension. If this is the main factor, it is expected that the TAB group on average will have a larger heat transfer improvement than the MEGA, and the degree of improvement will be similar within each group.

### 1.1.6 Solid-Liquid Interface Adsorption

The adsorption of surfactants to the solid surface has been empirically determined to follow particular patterns. When the adsorption is plotted against concentration, the result is an s-curve. This means that there is initially a very slow increase in adsorption at small concentrations, but as the concentration increases there is a point at which the adsorption suddenly increases dramatically for a short time before the
slope tapers off again at the higher level. The concentration of the dramatic increase has been called the critical hemimicelle concentration (CHC) and is similar to the CMC in that it is a threshold concentration above which the surfactant molecules arrange themselves differently. In this case they arrange themselves differently on the surface in a way that dramatically increases the amount of surfactant adsorbed to the surface. [11]

The CHC also scales with the CMC, since the driving forces that cause each are similar. Thus it is expected that lower CMC surfactants will have more adsorption and thus a higher contact angle for the same concentration.

1.2 Boiling

1.2.1 Boiling Curves

When the heat flux of boiling water is plotted against temperature, there is a distinct shape to the boiling curve that can be split into several regions, seen in Figure 1-1. The early part of the curve up to the first peak is the nucleate boiling phase. The first peak is the critical heat flux (CHF), which is the highest heat flux that can be achieved without film boiling. In industrial applications, film boiling is avoided, because film boiling involves a layer of vapor forming between the heating surface and the water, creating thermal insulation that allows the surface temperature to increase very rapidly and uncontrollably.

The CHF is the highest heat flux that can be obtained without very large temperatures because it the point at which the maximum number of nucleation sites are activated at the same time. There is a limit to the number of nucleation sites that can be activated at any one time because of the limited space. At some point, the surface reaches a limit of the number of distinct bubbles that can be growing at the same time and they begin to coalesce. This coalescence is called the film boiling regime. Once the nucleate bubbles have coalesced, there is a film of vapor separating the fluid from the surface, and the surface undergoes large increases in temperature before the
Figure 1-1: This is a representative boiling curve showing the approximate behavior of pure water. The phases discussed in the text can be seen here: the onset of boiling/nucleate boiling phase, the CHF point, and the film boiling regime. Dashed lines represent areas of the curve that are drastically different depending on the heating conditions and the whether the water is heating or cooling.

heat flux increases any more.

This study focuses on the nucleate boiling regime and the CHF of boiling water because these are the regions of the curve that are most applicable to industrial applications. Previous work has shown that the addition of surfactants to water drastically shifts the boiling curve and moves the CHF.

The shifting of the boiling curve would be useful because currently the boiling curve is fairly static. In industry, when using boiling for heat transfer, either the heat flux or the superheat can be optimized with different surface morphologies and wettabilities. The ability to control the shift of the boiling curve with surfactants would allow both the heat flux and the surface temperature to be controlled without remanufacturing, allowing for more flexible and precise chemical processing.
1.2.2 Homogenous vs Heterogeneous Nucleation

Water does not actually boil at 100°C at atmospheric pressure. At 100°C liquid water is in equilibrium with water vapor. However, in order to create bubbles in a pool of water, there is an energy of nucleation that must be overcome. The Gibbs free energy (ΔG) of homogenous bubble formation can be estimated by the equation [3]:

\[ ΔG = \frac{4}{3}πσ_1r_e^3 - \frac{4πσ_1}{3} \left[ 2 + \frac{1}{1 + \sigma_1/r_eP_l} \right] \left( \frac{r}{r_e} - 1 \right)^2 \] (1.4)

where \( σ \) is the surface tension at the interface, \( r \) is the radius, \( r_e \) is the radius at which the radius of the local maximum of \( ΔG \), and \( P_l \) is the pressure of the liquid. There is distinct energy required to create a bubble, so the temperature of the water must actually be more than 100°C in order to get nucleation. The difference between the actual temperature of the boiling water and 100°C is called the superheat.

There are two types of nucleation. Homogenous nucleation occurs in the bulk fluid without any sort of particle or surface to form upon. Heterogeneous nucleation occurs on the walls or particles and uses the energy of the water’s interaction with the surface to lower the energy required to nucleate. Homogenous nucleation almost never occurs in practice because it requires much more energy than heterogeneous nucleation.

1.2.3 Effect of Contact Angle on Boiling

The contact angle of a nucleating bubble on a heated surface makes a large difference in the amount of energy required for a bubble to form. This relationship can be seen in the following equation from classical nucleation theory [3]:

\[ ΔG_{het} = ΔG_{hom} \cos^4 \left( \frac{θ}{2} \right) (2 - \cos(θ)) \] (1.5)

where \( ΔG_{het} \) is the required energy for nucleation on the surface, \( ΔG_{hom} \) is the energy for bubbles to form homogeneously in the bulk fluid, and \( θ \) is the droplet
contact angle. This equation shows that increases in the contact angle lower the required energy for nucleation.

1.2.4 Nucleate Boiling

For a perfectly smooth surface, a large superheat, with temperatures of approximately 300°C, is required to overcome the free energy change to nucleate a bubble on the surface. This is not observed in practice. Real objects have surface features, some of which entrap microscopic pockets of gas that act as much lower energy nucleation sites. The geometry of these features also assists in bubble creation and growth because it changes the angles of solid-vapor-liquid contact and can lower the energy required to grow. [3]

1.2.5 Boiling Correlations

The boiling process is very difficult to analyze from fundamentals because it is so dependent on the exact surface structure and trapped gas, but there are correlations that can be used to determine approximate equations. In this study we are concerned about the approximate relationships between the quantities we are changing and measuring.

Cole and Rohsenow's correlation can be used to find the relationship between surface tension and bubble departure diameter \((D_b)\) [9):

\[
D_b \propto \sqrt{\gamma_{lv}}
\]  

(1.6)

To find the relationship between heat flux, the measured output, and all of the variables in this study, the Mikic-Rohsenow equations can be used [8][3]:

\[
q'' \propto D_b^3 \left( \frac{\Omega(\theta)}{\gamma_{lv}} \right)^m \Delta T^{m+1}
\]  

(1.7)

Where \(q''\) is the heat flux, the constant \(m\) is empirically determined to be 6 in most cases, \(\gamma_{lv}\) is the dynamic surface tension found in equation 1.6. \(\Delta T\) is the difference
between the surface temperature and the saturation temperature, so it is the applied superheat that is varied to obtain the boiling curve. $\Omega$ is the geometric nucleation parameter and is a function of $\theta$ [6]. $\theta$ is the liquid vapor initial contact angle, and is heavily changed by the presence of surfactants. $\Omega$ is positively correlated with $\theta$, so increases in $\theta$ increase the heat flux of the system.

Figure 1-2 shows the effect of increasing contact angle. For any given $\phi$, which is a function of the surface texture, the ratio of activated nucleation sites increases with the contact angle.
Chapter 2

Experimental Setup and Methods

2.1 Setup

Figure 2-1 shows the experimental setup for this study. A glass chamber was filled with 400 mL of DI water. At the base of the glass chamber is a silver foil base. The foil is roughed with 240-grit sandpaper to increase nucleation sites and soldered to the copper block. The copper block with a cross sectional area of 4 cm$^2$ has four embedded thermocouples to determine the heat flux into the water. The cartridge heater sits underneath the copper block and is powered by a programmable power supply that is controlled by LabView. The condenser at the top condensed the vapor to maintain a closed system. The rope heaters kept the bulk fluid saturated during runs. A Phantom V7 high speed camera was used to record video of the boiling with Vision Research software.
The four thermocouples are placed 8 mm apart, their measured temperatures are used to solve the following fin equation for the heat flux at the surface of the copper block:

\[ 0 = \frac{\partial^2 T(x)}{\partial x^2} - \frac{hP}{kA} ((Tx) - T_\infty) \]  

(2.1)

Where \( h \) is the heat transfer coefficient, \( P \) is the perimeter of the copper block, \( k \) is the thermal conductivity of the copper block, \( A \) is the area of the copper block and \( T_\infty \) is the ambient temperature. The boundary conditions used are \( \left( \frac{\partial T}{\partial x} \right)_{x=L} = \frac{q^f}{k} \) and \( T(x = 0) = T_{surface} \) where an arbitrary value of \( L \) was used and \( q^f \) and \( h \) are used as fitting parameters.
2.2 Methods

At the beginning of each set of experiments, the water was warmed up and degassed by boiling vigorously for five minutes. Then two boiling curves were measured at the same concentration to make sure that the system was fully degassed and in equilibrium. Each boiling curve measurement was preceded by a warmup run to ensure that the bulk fluid was completely saturated. For a warmup, 200 or 400 W were applied to the heater until the bulk fluid began boiling. The power was then shut off and the liquid cooled to approximately 103°C before the run was started.

For the boiling curve measurements, both the rising temperature and falling temperature curves were measured. The decreasing temperature curves were used for analysis because they did not have the jumps that initial nucleation causes. For the rising temperature curve, a linear power ramp that ran from 0 W to 800 W over the course of 1200 seconds was programmed into LabView. The water was heated at this power ramp until it either hit 70 W cm\(^{-2}\) or the CHF. At this point, the power was cut off manually and the heat flux and temperature were continued to be measured as the water and copper block cooled.

Solutions of 173 mM of each surfactant were mixed. In between runs, the water was cooled to below saturation temperature and surfactant was added to the water. 100 \(\mu\)L, 250 \(\mu\)L, and 10 mL syringes were used to add surfactant. In between experiments with different surfactants, the entire experimental setup was rinsed thoroughly with distilled water to prevent contamination.
2.3 Concentrations Tested

Table 2.1 lists all concentrations tested in this study. Most of the concentrations were tested once. Anything tested more than once was tested several times for calibration purposes.

<table>
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<td>3.460</td>
<td>5.190</td>
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<td>4.325</td>
<td>6.055</td>
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<td>5.190</td>
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</tbody>
</table>

Table 2.1: This table shows all concentrations of each surfactant that were tested in this study. The concentrations tested were adjusted based on the amount of shifting that was seen at previous concentrations. All surfactants start out with very small concentration jumps, since they all saw a lot of curve shifting early on. Jumps were than decreased as shifting slowed. Two of the surfactants, MEGA-10 and 14TAB, reached their CMCs in this study.
Chapter 3

Results

3.1 Initial Data

Figure 3-1 shows the general trends of the changes in the boiling curve with increasing concentration for MEGA-10. The rightmost black line is the boiling curve of pure water. With initial small additions of the surfactant the boiling curve shifts left slightly, but the CHF remains outside of the range of heat fluxes in this study. As concentration increases to higher values, the curve continues to shift left and the CHF lowers to point where it is captured. The curve continues to shift left and the CHF flux continues to lower until it reaches a saturation point and both cease to change.

All of the surfactants exhibited similar behavior. The major differences between surfactants are the amount of surfactant it took to cause these shifts and the exact shape of the curve. Initial data graphs for all other surfactants can be found in the appendix section A.2, later results sections will characterize the relationship between the shifts and the concentration of each surfactant.
Figure 3-1: This shows the MEGA-10 heat flux vs temperature for various concentrations. The shifting of the boiling curve with the addition of surfactant can be seen here.

3.2 Heat Flux Trends

3.2.1 General Trends

For the first level of analysis in this study, particular heat fluxes were chosen and the temperature of the water was plotted for each concentration of surfactant. In MEGA-10, shown in Figure 3-2, there is an initial steep slope where the temperature changes greatly for each additional bit of surfactant, but it tapers off as the concentration increases. In general, it appears that lower flux curves flatten out at lower concentra-
Figure 3-2: Temperature vs concentration for MEGA-10 is plotted for particular heat fluxes to show how increasing concentration depresses temperature.
tions than higher flux curves. There is also a pattern that at lower concentrations, a higher flux leads to a higher temperature, but at higher concentrations this is no longer true. This is consistent with the shape change of the boiling curve that occurs along with the shifting of the curve.

All of the other surfactants show similar patterns in their temperature vs concentration curves for different heat fluxes. These plots can be found in section B.1 of the appendix. Later sections will directly compare the results from different surfactants.
Figure 3-3: This figure plots the temperature vs. absolute concentration curves for all surfactants at 10 W cm$^{-2}$.

### 3.2.2 Comparison of Different Surfactants

Figures 3-3 and 3-4 show that the general trends of initial strong slope and flattening after saturation is consistent with different surfactants. The slopes at low concentration do not seem at all related to the CMC. At larger concentrations, plotting as a percentage of CMC seems to normalize the curves and each group converges, which shows some dependence on the CMC.

Within the MEGA and TAB groups temperature suppression increases with length of chain. This is consistent with the theory that adsorption onto the boiling surface is the primary mechanism for boiling improvement. The longer molecules have more
carbon, which makes them more hydrophobic. When they adsorb onto the surface, they increase the contact angle between a nucleating bubble and the surface, and decrease the nucleation energy required. Lower nucleation energy means a lower superheat required in order to get nucleation. The slopes and magnitude of the changes are consistent with the theory that solid-liquid adsorption is approximately proportional with the concentration up to the CMC, so smaller CMC surfactants will have a lot more surfactants on the solid-liquid interface compared to larger CMC surfactants for the same absolute concentration.

We did not run multiple tests for every concentration, so there is some uncertainty in our measurements. We did run multiple measurements for a few concentrations with a few days in between tests. For these tests we found shifts of up to 1°C. There is approximately a 0.1°C uncertainty in the thermocouple measurements. There is also an uncertainty that comes from time averaging the data. The temperature can fluctuate up to 1°C. Combining these error by Pythagorean sum gives a total error of approximately 1°C.
Figure 3-4: This figure plots the temperature vs. percentage of CMC curves for all surfactants at 10 W cm\(^{-2}\). This can be compared with Figure 3-3 to see if there are any significant trends that appear to be related to CMC.
Figure 3-5: This figure plots the critical heat flux vs. concentration for all surfactants. For each of these surfactants, CHF exists at the lower concentrations, but where it is not on the plot, it was too high to be captured by this study’s set of experiments.

3.3 CHF Trends

The critical heat flux follows similar trends to the temperature at particular fluxes. It has an initial drop-off and flattens out after it hits some amount of concentration. In both groups, the CHF suppression is larger for the longer chains. This fits with the argument that greater hydrophobicity of the surface is one of the driving forces for this change. Since the contact angle is so much greater, the nucleating bubbles are more spread across the surface. This means that there can be less sites activated before the bubbles start coalescing and the boiling begins to transition into film boiling. The
Figure 3-6: This figure plots the low concentration portion of the 20 W cm$^{-2}$ temperature vs concentration curves for different surfactants with the linear fit of each curve. Solid lines are the original curves and the dotted lines are the linear fits.

The lower number of maximum activated sites is shown in the lower critical heat flux.

### 3.4 Early Slope of Temperature vs Concentration Curves

The lower concentration, quasi-linear portions of the particular heat flux curves are shown in Figure 3-5. This is a portion of Figure B-8 in the appendix. A linear fit was applied to the low concentration sections of the curve to try to determine the
scale of the difference between surfactants in early curve shifting. Figure 3-6 plots these slopes for different heat fluxes. Figures of the low concentration data and their linear fits for different heat fluxes can be found in appendix section B.2.3. Since each curve starts at around the same point, greater slopes suggest greater suppression of temperature for that heat flux. The precision of these slope measurements is very low since there aren’t a lot of data points for this section, but it does generally follow the trends commented upon earlier that the temperature is lower for the longer-chained surfactants.

The slopes in this early portion of the curve suggest that the diffusivity has a role to play in the changes resulting from low concentrations. The slopes are generally grouped into the TAB group and the MEGA group. These groups do not have large differences in their chain lengths or their hydrophobicity, but due to their large difference in head size they have a large difference in diffusivity (see section 1.1.5). Equations 1.1, 1.2, and 1.7 support this because $\Delta T^{-(m+1)}$ should be proportional to $1/\gamma_{lv}^m$. 
3.5 Qualitative Look at Boiling Change

In Figure 3-7, the qualitative differences in boiling between low concentration of surfactant and high concentration of surfactant can be seen. For the same heat flux, high concentrations of the surfactants tested show higher nucleation density than pure water. This can be seen by the number of bubbles and the total amount of vapor. All the high surfactant cases also have much smaller bubbles, this has two reasons. The first is that the lower surface tension in the surfactant filled water means that there is less force holding the bubbles to the surface, so the buoyant force of the vapor has less force to overcome and thus have less vapor enclosed in the bubble before it breaks from the surface. The second is that in pure water, bubbles that bump into each other on their rise tend to coalesce. In higher surfactant solutions, there is a concentration of surfactant on the surface of the bubbles, and that surfactant prevents the bubbles
Figure 3-8: All at 10 W cm\(^{-2}\). a) MEGA-8 at 0.054 mM, b) MEGA-8 at 6.05 mM, c) MEGA-10 at 0 mM, d) MEGA-10 at 5.19 mM, e) 10TAB at 0 mM, f) 10TAB at 5.19 mM, g) 12TAB at 0.043 mM, h) 12TAB at 4.325 mM, i) 14TAB at 0 mM, j) 14TAB at 5.19 mM
Figure 3-9: This figure shows the measurement of the advancing contact angle of pure water (75.2°). [10] The substrate is smooth copper polished with 1 μm polishing paper.

from coalescing. Both of these factors combine to have a significant difference in the size of the bubbles.

The one thing that cannot be observed in just these pictures is the contact angle of the nucleating bubble. The nucleation and separation from the surface happens too quickly to reasonably be able to catch and analyze with this experimental setup. Increases in the contact angle can be seen in a separate experiment shown in Figures 3-9 and 3-10 [10]. There the addition of 2.6 mM of 12TAB to pure water increased the contact angle by 10°. This is consistent with the hypothesis that surfactants adsorbing to the surface and making it more hydrophobic is the driving force for the changes in boiling, because an increase in the advancing contact angle is characteristic of an increase in the hydrophobicity of a surface.
Figure 3-10: This figure shows the measurement of the advancing contact angle of water with 2.6mM 12TAB (85.0°) [10]. The substrate is the same smooth copper polished with 1 μm polishing paper seen in figure 3-9. This provides support for the hypothesis that the surfactant is making the surface more hydrophobic.
Chapter 4

Conclusions

In this study, the boiling improvement capabilities of surfactants from the MEGA series and the TAB series were explored. The addition of these surfactants to boiling water was found to lower the superheat for particular fluxes by up to 55%. There was also a significant suppression of the heat flux at these high concentrations. High concentrations of MEGA and TAB series surfactants seems ideal if the goal is moderate heat flux at very low superheat.

The comparison of the shifting of the boiling curves with increasing concentration for the different surfactants gives additional support for hypotheses about the driving mechanisms for the changes in the boiling curve. The shifting that occurs at low concentrations of surfactant seem correlated with the diffusivities of the different surfactants. The large shifting that occurs at larger concentrations is no longer correlated with the diffusivities, but it is correlated with the hydrophobic tail length of each of the surfactants. This supports the hypothesis that the lowering of the dynamic surface tension, which is correlated to the diffusivity of the surfactants, is responsible for part of the lowering of the superheat. However, the dynamic surface tension changes that can occur in the small growth lifetime of a bubble cannot account for all of the shifting of the boiling curve that occurs. The fact that the larger shifting is correlated with the hydrophobic tail length supports the hypothesis that part of the shifting occurs due to the surfactants adsorbing onto the surface, making it more hydrophobic, increasing the contact angle, and decreasing the nucleation energy.
This study has shown some of the changes to the boiling curve that can be made by the addition of particular surfactants. It has given some insight into the actual changes that occur. More studies should be done to validate the findings of this study and to give more certainty of how surfactant concentration changes the energy of nucleation and the heat transfer of a system. This study consisted of a nonionic and a cationic homologous series, so studies of anionic groups should be performed to assess the influence of particle charges. Studies of groups with different head sizes and diffusion coefficients should be made to assess the diffusion limited hypothesis at low absolute concentration. We were also unable to measure the boiling curve of the high-CMC surfactants all the way up to their CMC concentration, future studies should increase the number of concentrations to assess the solid-liquid absorption hypothesis. With further study, engineers in the industry could be able to decide a particular heat flux and superheat they want, and know exactly the amount and type of surfactant they can add to their system to successfully adapt the boiling curve to their needs.
Appendix A

Initial Data

A.1 Note on Vertical Jumps

In some of the concentration vs temperature graphs, vertical jumps can be seen. These jumps are the result of the fact that sometimes it was necessary to pause an experiment overnight. This gave time for diffusion to change the nature of some of the initial nucleation spots. In some cases, nucleation spots were destroyed, likely by the entrapped gas in them diffusing into the fluid. In others, nucleation spots were created, possibly by gas diffusing out and collecting there when the fluid was de-gassed as part of the warm-up.

Although there are jumps, each data point is an equilibrium curve for the day. Any time the first curve of the day did not match the curve from the day before, additional runs were performed to ensure that the system was indeed fully de-gassed and in equilibrium. Only equilibrium curves are included as data points.

This shows some of the uncertainty involved in boiling experiments. Changes in nucleation sites that were not reasonably controllable shifted some of the boiling curves. However, these shifts were not large enough to obscure the overall trends of the results.

A.2 Boiling Curve Plots
Figure A-1: This shows the MEGA-10 heat flux vs temperature for various concentrations. The shifting of the boiling curve with the addition of surfactant can be seen here.
Figure A-2: This shows the MEGA-8 heat flux vs temperature for various concentrations. The shifting of the boiling curve with the addition of surfactant can be seen here.
Figure A-3: This shows the 12TAB heat flux vs temperature for various concentrations. The shifting of the boiling curve with the addition of surfactant can be seen here.
Figure A-4: This shows the 10TAB heat flux vs temperature for various concentrations. The shifting of the boiling curve with the addition of surfactant can be seen here.
Figure A-5: This shows the 14TAB heat flux vs temperature for various concentrations. The shifting of the boiling curve with the addition of surfactant can be seen here.
Appendix B

Temperature vs. Concentration Plots
B.1 Single Surfactant Plots

Figure B-1: Temperature vs concentration for MEGA-10 is plotted for particular heat fluxes to show how increasing concentration depresses temperature.
Figure B-2: Temperature vs concentration for MEGA-8 is plotted for particular heat fluxes to show how increasing concentration depresses temperature.
Figure B-3: Temperature vs concentration for 12TAB is plotted for particular heat fluxes to show how increasing concentration depresses temperature. Vertical jumps in the plot are explained in section A.1.
Figure B-4: Temperature vs concentration for 10TAB is plotted for particular heat fluxes to show how increasing concentration depresses temperature. Vertical jumps in the plot are explained in section A.1.
Figure B-5: Temperature vs concentration for 14TAB is plotted for particular heat fluxes to show how increasing concentration depresses temperature.
B.2 Multiple Surfactants Compared

B.2.1 Absolute Concentration

Figure B-6: This figure plots the temperature vs. concentration curves for all surfactants at 5 W cm\(^{-2}\). This allows for comparison across surfactants. Vertical jumps in the plot are explained in section A.1.
Figure B-7: This figure plots the temperature vs. concentration curves for all surfactants at 10 W cm\(^{-2}\). This allows for comparison across surfactants. Vertical jumps in the plot are explained in section A.1.
Figure B-8: This figure plots the temperature vs. concentration curves for all surfactants at 20 W cm$^{-2}$. This allows for comparison across surfactants. Vertical jumps in the plot are explained in section A.1.
Figure B-9: This figure plots the temperature vs. concentration curves for all surfactants at 30 W cm$^{-2}$. This allows for comparison across surfactants. Vertical jumps in the plot are explained in section A.1.
Figure B-10: This figure plots the temperature vs. Percentage of CMC curves for all surfactants at 5 W cm$^{-2}$. This allows for comparison across surfactants. Vertical jumps in the plot are explained in section A.1.
Figure B-11: This figure plots the temperature vs. Percentage of CMC curves for all surfactants at 10Wcm$^{-2}$. This allows for comparison across surfactants. Vertical jumps in the plot are explained in section A.1.
Figure B-12: This figure plots the temperature vs. Percentage of CMC curves for all surfactants at 20 W cm$^{-2}$. This allows for comparison across surfactants. Vertical jumps in the plot are explained in section A.1.
Figure B-13: This figure plots the temperature vs. Percentage of CMC curves for all surfactants at 30 W cm$^{-2}$. This allows for comparison across surfactants. Vertical jumps in the plot are explained in section A.1.
B.2.3 Linear Fit Plots

Figure B-14: This figure plots the low concentration portion of the 5 W cm\(^{-2}\) temperature vs concentration curves for different surfactants with the linear fit of each curve. This plot is a subsection of Figure B-6.
Figure B-15: This figure plots the low concentration portion of the 10 W cm$^{-2}$ temperature vs concentration curves for different surfactants with the linear fit of each curve. This plot is a subsection of Figure B-7.
Figure B-16: This figure plots the low concentration portion of the 20 W cm$^{-2}$ temperature vs concentration curves for different surfactants with the linear fit of each curve. This plot is a subsection of Figure B-8.
Figure B-17: This figure plots the low concentration portion of the 30 W cm$^{-2}$ temperature vs concentration curves for different surfactants with the linear fit of each curve. This plot is a subsection of Figure B-9.
Bibliography


