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The Effect of a Surfactant Monolayer on Gas Exchange Across an Air-Water Interface during Mixed Convection

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The Effect of a Surfactant Monolayer on Gas Exchange Across an Air-Water Interface during Mixed Convection

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the Graduate School of
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In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Mechanical Engineering

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Abstract

A set of laboratory experiments are presented that reveal the effect of a surfactant monolayer on the transport of oxygen across an air-water interface during mixed convection conditions. The experiments were conducted in a wind/water tunnel with water tanks of differing depth. Forced convection was imposed via the air flow, while natural convection was imposed by heating the water bulk above the air temperature. For the range of wind speeds being considered, mixed convection conditions resulted. Experiments were also conducted with only forced convection present. The data acquired during these experiments were used to develop a parameterization between the Sherwood number for oxygen transport ($Sh$) and the Reynolds ($Re$), Rayleigh ($Ra$), and Schmidt ($Sc$) numbers. This parameterization was obtained for the case of a clean water surface and for a water surface covered with one of two surfactant monolayers, controlled (oleyl alcohol) and uncontrolled (indigenous). The data reveal that, at a given $Ra$, the presence of a surfactant monolayer reduces the value of $Sh$ by approximately one order of magnitude. This reduction is caused by the reduction of subsurface turbulence caused by the presence of the surfactant monolayer. The data also show that $Sh$ was relatively insensitive to $Re$ and $Sc$ when a surfactant monolayer was present, which is verified by the forced convection only results. However, $Sh$ was dependent on $Ra$, $Re$, and $Sc$ for the clean water surface condition. For the two surfactant conditions, no change in behavior of the gas exchange was noticed. The elasticity of the air-water interface which results from the presence of a surfactant is used to explain the difference between clean surface and surfactant-covered results. The elasticity imparted by a surfactant monolayer is also used to explain the similarity of the results for the two surfactants. For both the clean and surfactant cases, $Sh$ increases with $Ra$. 
Dedication

To my parents, who always encouraged and never inhibited my intellectual growth and maturation.
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Chapter 1

Introduction

1.1 Gas Exchange

The transport of dissolved gases such as oxygen and carbon dioxide across an air-water interface, hereafter referred to as gas exchange, is crucial to the ecology of lakes, streams and oceans. Indeed, for aquatic life, especially fish, a minimum dissolved oxygen concentration of $\sim 2$ mg/L is required to maintain life[29]. Many factors influence this transport process including wind and the subsurface turbulence generated by wind[34, 37, 9, 8, 14, 27, 7, 24, 10, 44, 49], breaking waves and the concomitant effects of bubbles[8, 6, 27, 37, 5], capillary waves[8, 6, 27, 37, 40, 34, 26, 48, 54], natural convection[36, 41, 15], rain[23, 24], and chemical reactions within water[52, 53, 48, 50], to name just a few.

Gas exchange can be enhanced by wind and subsurface turbulence generated by wind. At relatively low wind speeds (under $\sim 3 - 4$ m/s), prior research shows that subsurface turbulence caused by wind shear alone enhances gas exchange[34, 37, 9, 8, 14, 27, 7, 24, 10]. However, this same research has shown that the relationship between wind speed and gas exchange enhancement is weak, so much so that some consider the mass transfer coefficient to be constant at these wind speeds[37, 9, 27, 34, 8, 7, 10]. Most considered the mass transfer coefficient to be constant below $\sim 3 - 4$ m/s. Additional turbulence in the bulk beyond that caused by wind shear, such as that resulting from stirrers, shear at the bottom of a moving stream, and recirculation pumps, has been shown to further enhance gas exchange[7, 37, 8]. These studies have shown that the subsurface turbulence at the air-water interface is the controlling factor for gas exchange when the water surface
is smooth and the water bulk is free of bubbles[37, 27, 14, 10, 7, 24].

At higher wind speeds, above $\sim 10$ m/s, wind shear causes breaking waves, spray, and subsequent entrainment of bubbles within the water bulk. These factors dominate gas exchange by increasing the surface area of the air-water interface, as well as possibly disturbing the water surface diffusive sublayer[8, 6, 27, 37, 5]. Bubbles, in particular, have been shown to significantly enhance gas exchange due to increasing surface area and pressure[5, 37].

At moderate wind speeds, those between $\sim 3 - 4$ m/s and $\sim 10$ m/s, wind shear causes capillary waves that impact gas exchange[22]. The onset of capillary waves has been shown to significantly enhance gas exchange, compared to wind shear alone[37, 27, 8, 34]. This increase in the effectiveness of gas exchange due to capillary waves has been attributed to an increase of surface area and the increase of sub-surface turbulence in the water due to greater energy at the surface[37, 27, 8, 34, 5, 26, 40, 48, 54].

Rain has also been shown to increase gas exchange across the air-water interface[24, 23]. The primary transport processes are similar to that of high wind speeds: bubble formation, increase of subsurface turbulence, and a breakdown of the diffusive sublayer[24].

Gas exchange can be affected by chemical reactions in water[52, 53, 48, 50]. These reactions have been shown primarily to enhance gas exchange across the air-water interface. This is achieved by reactions reducing the concentration of the gas within the water, thereby increasing the concentration gradient leading to an increase in the magnitude of gas exchange[53, 48, 50].

These various phenomena all have the effect of enhancing gas exchange. Moreover, they all influence gas exchange on the water side of the air-water interface. Indeed, the studies presented above show that the water side, not the air side, is the controlling facet in gas exchange across an air-water interface, a point that will be explicitly demonstrated later in this thesis.

1.2 Mixed Convection

Herein, transport of oxygen across an air-water interface under the specific case of mixed convection conditions is considered. Gas exchange during mixed convection is the situation where transport due to both natural convection and forced convection is significant, and not dominated by either. While such situations are not common on the surface of the ocean where the globally averaged wind speed is $\sim 7$ m/s (e.g. Thomas et al.[46]), for lakes, ponds and other small inland water bodies,
wind speeds are much smaller. Studies by Lenters[33], Klink[30], and Deaves & Lines[13] found that the average wind speed over various lakes and land masses in the United States and United Kingdom is less than \( \sim 3 \) m/s.

By using a heat transfer/mass transfer analogy, it is possible to develop an order of magnitude analysis to determine whether mixed convection conditions exist. One example of this order of magnitude analysis is Bejan’s[4] analysis to determine mixed convection conditions for a heated vertical wall with concurrent airflow. The resulting boundary layer thicknesses are:

\[
\delta_{h,F} \sim yRe^{-1/2}Pr^{-1/3}
\] (1.1)

for forced convection and:

\[
\delta_{h,N} \sim yRa^{-1/4}
\] (1.2)

for natural convection, where \( \delta_{h,F} \) is the thermal boundary layer thickness under forced convection; \( y \), the height of the wall; and \( \delta_{h,N} \), the thermal boundary layer thickness under natural convection.

The ratio of the thermal boundary layer thicknesses determines the dominant form of convection within the system:

\[
\frac{\delta_{h,F}}{\delta_{h,N}} = \frac{Ra^{1/4}}{Re^{1/2}Pr^{1/3}}
\] (1.3)

Natural convection dominates when the ratio is \( > O(1) \), forced convection dominates when the ratio is \( < O(1) \), and mixed convection exists when the ratio is \( O(1) \).

In the system considered here, mass transfer is being studied as opposed to heat transfer. The heat transfer/mass transfer analogy, in which \( Sc \) takes the place of \( Pr \), is applied and the mass transfer boundary layer is assumed to develop on the water side of the air-water interface. As this interface is horizontal instead of vertical, simply applying the heat/mass transfer analogy to Eqs. (1.1) & (1.2) is not sufficient to characterize the boundary layer thicknesses and modifications must be made. For forced convection, the modification is simple. In addition to application of the heat/mass transfer analogy to the classical laminar flat plate relationship, a horizontal length scale
is used. Hence, the mass transfer boundary layer thickness for forced convection is:

$$\delta_F \sim LRe_F^{-1/2}Sc^{-1/3}$$  \hspace{1cm} (1.4)$$

where the characteristic length for $Re_F$ is the tank length $L$, and the water velocity is taken as 5% of the wind speed[27].

In Eq. (1.2), the Rayleigh number ($Ra$) is used in the characterization of the growth of the natural convection boundary layer. In Bejan’s work[4] $Ra$ is defined using a vertical length scale. In the system under consideration, $Ra$ is still defined vertically, because that is where the temperature difference driving natural convection occurs (bulk water to water surface). An order of magnitude estimate of the natural convection velocity combined via a balance between the kinetic energy and the buoyancy of the fluid, following the treatment of Oosthuizen & Naylor[38]:

$$\frac{1}{2} \rho u_N^2 = \beta g \rho (\Delta T) d$$  \hspace{1cm} (1.5)$$

which gives:

$$u_N = \sqrt{\beta g \Delta T d}$$  \hspace{1cm} (1.6)$$

where $u_N$ is the velocity resulting from natural convection; $\rho$, the density of the fluid; $\beta$, the coefficient of volumetric expansion; $g$, gravitational acceleration; $\Delta T$, the temperature difference between the surface and fluid bulk; and $d$, the depth of the tank. Assuming that this is the velocity at the water surface, a form of the boundary layer thickness similar to that found in Eq. (1.4) can be used for natural convection:

$$\delta_N \sim LRe_N^{-1/2}Sc^{-1/3}$$  \hspace{1cm} (1.7)$$

where the characteristic length used for $Re_N$ is the tank length $L$.

When the ratio $\delta_F/\delta_N$ is of order unity, mixed convection conditions exist. This ratio is:

$$\frac{\delta_F}{\delta_N} = \frac{Re_N^{1/2}}{Re_F^{1/2}} = \frac{u_N^{1/2}}{u_F^{1/2}}$$  \hspace{1cm} (1.8)$$

Using water side properties when computing the dimensionless quantities, and assuming a charac-
teristic $\Delta T$ of 1 K, gives $\delta_F/\delta_N = 5.7$ when $U = 1 \text{ m/s}$ at a water temperature of 25°C and an extreme value for lake depth of $d = 1000 \text{ m}$. Keeping the same parameters, but using a shallower depth, $d = 10 \text{ m}$, typical of small lakes[15] gives $\delta_F/\delta_N = 1.8$. In both cases, $\delta_F/\delta_N$ is of order unity. Hence, for wind speeds typical of lakes, gas exchange is a mixed convection problem. For our experimental facility, typical values of $\Delta T$ are $\sim 1 \text{ K}$, $d$ ranges from 0.076 to 0.381 m, and the wind speed ranges from $U = 1$ to 4 m/s. This gives $\delta_F/\delta_N = 0.28$ at a minimum to 0.84 at a maximum, showing that mixed convection conditions exists in our experimental facility as well.

While significant research has been conducted on gas exchange due to natural convection alone, and forced convection alone, few studies have been conducted on gas exchange across an air-water interface during mixed convection. Jähne noted that water that is warmer than the air above it noticeably increases the mass transfer coefficient of CO$_2$[26], however the wind speed conditions of this study are unclear. In a field study of the ocean, McNeil & Merlivat observed that natural convection had a significant impact on CO$_2$ transport at wind speeds of 4 to 5 m/s, measured 10 m above the ocean surface[36]. Laboratory research performed by Schladow et al. showed that natural convection can increase the mass transfer coefficient of oxygen by 9% to 40% at a wind speed of 0.1 m/s [41]. Natural convection was shown to have a larger impact on gas exchange at low wind speeds in a study of CO$_2$ transport in the ocean[51], while a later study suggested that this effect is most important at wind speeds less than 1 m/s[55]. In field research of gas transfer in the ocean, water-side convection at low and moderate wind speeds ($< 6 \text{ m/s}$) was concluded to be a dominating mechanism controlling the gas transfer of CO$_2$, as a correlation to only wind speed did not predict gas transfer well[18, 28], which was suggested by previous research concerning wind speeds over lakes[10]. These studies show that each of forced and natural convection act to enhance gas exchange across the air water interface, but none investigate their combined impact.

The paucity of research on gas exchange across an air-water interface during mixed convection conditions is one of the motivations of the present study. Moreover, since most of the above studies were conducted in the field, it would be beneficial to have laboratory studies where more controlled conditions can be used to elucidate the effects of forced convection, natural convection, and as will be discussed below, the presence of surfactant monolayers.
1.3 Surfactants

In any air-water transport problem, surfactant monolayers can be an important factor. Surfactant monolayers are molecule-thick films that collect at the air-water interface\[3\]. These materials tend to collect at the water surface due to their chemistry: one part of the molecule that is hydrophilic (water soluble) and another that is hydrophobic (insoluble in water). The hydrophobic end of the surfactant molecule drives it out of the water, but the hydrophilic end keeps the molecule from escaping from the water surface\[12\]. Like other materials, surfactant monolayers can exist in various phases, including gas, liquid, and solid. In gaseous surfactants, molecules are spread far enough apart that they exert little force upon each other. They are, though, restricted to the surface such that molecular motion is two-dimensional as opposed to actual gases, which exhibit three-dimensional kinetic motion\[20\]. Surfactant monolayers in the liquid phase have molecules that are packed to a much greater degree than those in a gaseous monolayer, such that intermolecular forces become significant, though the molecules are able to move about the water surface\[20\]. Solid phase monolayers are surfactants in which its molecules have been packed as closely as possible, resembling a two-dimensional crystalline structure\[20\]. A surfactant is able to change phases like other materials as well. At a high enough temperature, a solid phase monolayer can lose its coherence and “melt” two-dimensionally into a liquid phase monolayer\[12\].

Surfactants also have various levels of solubility in the bulk liquid. Though both soluble and insoluble surfactants act at the water surface, they differ in how they form and react to compression. Insoluble surfactants have a very limited solubility in the bulk liquid and tend to accumulate on the water surface\[12\]. Insoluble surfactants also tend to spread across the water surface when a clean water surface is exposed, to the point that equilibrium is kept between the surfactant on the surface and in the bulk\[20\]. Furthermore, when the monolayer is compressed, it exerts a finite force outward in order to restore equilibrium conditions\[12, 20\]. Soluble surfactants, also referred to as adsorbed surfactants, are materials that exist in solution in the water bulk as well as on the water surface\[20\]. These materials lower the energy of the water surface, and thereby tend to diffuse from the bulk to a higher concentration at the surface\[12\]. Since the monolayer is maintained by equilibrium of the rates of diffusion of molecules to and from the water surface, compression of the monolayer will not result in a restorative force, but will simply force molecules from the surface into the bulk\[20\].

The surfactants that will be investigated here are insoluble and liquid phase. Surfactant
monolayers also change some of the properties of the air-water interface, in particular, surface tension and the hydrodynamic boundary condition. The surface tension of a free water surface with a surfactant is generally less than that of the clean free water surface[20]. This difference in surface tension is called the spreading (or surface) pressure of the surfactant monolayer:

\[
\Pi = \gamma_0 - \gamma
\]  

(1.9)

where \(\gamma_0\) is the surface tension of the clean water surface and \(\gamma\) is the surface tension of the surface with the surfactant monolayer present. The equilibrium spreading pressure is, then, the pressure at which the surfactant monolayer is in dynamic equilibrium with the surfactant in the bulk[20].

Another effect of the presence of a surfactant monolayer is a change in the hydrodynamic boundary condition. For the surfactant studied here, the presence of an insoluble liquid phase monolayer results in a constant elasticity boundary condition on the water-side of the air-water interface, as opposed to a shear-free boundary condition for a clean water surface[17]. The Gibbs equation for elasticity shows that the elasticity is dependent on the resistance to change of the surface area of the monolayer:

\[
E = 2A \frac{d\gamma}{dA}
\]  

(1.10)

where \(A\) is the surface area.

This elasticity at the water surface influences motion at both the air and water sides of the interface. On the water side, as fluid parcels move near the surface, they tend to carry surfactant molecules with them which compresses part of the monolayer. The monolayer responds by exerting a back pressure in order to return to its equilibrium state[12], which is illustrated in Fig. 1.1. Similarly, wind shear that would move surface water parcels essentially without resistance at a clean water surface faces resistance from a surfactant monolayer. As is illustrated in Fig. 1.2, wind shear compresses the monolayer, which resists this by exerting a back pressure to restore equilibrium[12].

For the liquid phase surfactants considered here, the monolayer’s impact on gas exchange occurs by damping the subsurface turbulence rather than by creating a barrier through which gas cannot cross[12, 11, 19, 2, 32]. When water is subjected to wind stress, surfactants have been shown to decrease the mass transfer due to the damping of subsurface turbulence[6, 35]. Goldman et al.[21] performed experiments using surfactants such as oleyl alcohol and found a 50% decrease
in the mass transfer coefficient of oxygen compared to a clean surface for the case of mechanically 
induced turbulence, a result that they attributed to the damping of subsurface turbulence and an 
associated reduction in surface renewal by the surfactant. In the research presented here, the effect 
that surfactants have on oxygen transport is investigated for mixed convection conditions. This has 
not been addressed prior to this work. This study is further motivated by the multiple effects that 
surfactants can have in this situation. Surfactants restrict motion of the surface fluid at the interface. 
Hence, mixing of the water bulk will be reduced in the presence of a surfactant, which should result 
in a reduced oxygen transport rate. However, at the same time, this restriction of surface motion 
can be expected to result in greater cooling of the water surface. This is because the monolayer, 
in restricting surface motion, forces surface liquid to be subjected to air cooling for a longer period 
of time, decreasing the surface temperature, thereby increasing the intensity of natural convection 
which should increase oxygen transport. Finally, however, any water-side natural convection will 
again be restricted near the interface by the presence of the monolayer, reducing transport. This 
complex set of interactions further motivates the present study.
1.4 Development from Theory

The system considered here consists of an insulated water body with a free water surface in contact with air as illustrated in Fig. 1.3. The mass flux of oxygen is into the water bulk, and the water temperature is greater than that of the air, creating natural convection conditions within the water. Forced convection also occurs, due to the flow of air over the water surface.

The goal of this work is to develop a relationship between the dimensionless groups relevant to oxygen exchange across the air-water interface: the Reynolds, Rayleigh, Schmidt, and Sherwood numbers. Specifically, the Sherwood number will be parameterized in terms of the Rayleigh, Reynolds, and Schmidt numbers:

$$Sh = f(Ra, Re, Sc)$$  

where $Sh$ is the Sherwood number; $Ra$, the Rayleigh number; $Re$, the Reynolds number; and $Sc$, the Schmidt number.
Figure 1.3: Illustration of system under consideration
the Schmidt number. These are defined as:

\[
Sh = \frac{k_L d}{D} \quad (1.12)
\]

\[
Re = \frac{UL}{\nu} \quad (1.13)
\]

\[
Ra = \frac{g \beta (T_b - T_s) d^3}{\alpha \nu} \quad (1.14)
\]

\[
Sc = \frac{\nu}{D} \quad (1.15)
\]

where \(U\) is the characteristic velocity; \(L\), the characteristic downstream length; \(\nu\), the kinematic viscosity of water; \(g\), gravitational acceleration; \(\beta\), the volume expansion coefficient; \(T_b\), the bulk water temperature; \(T_s\), the surface water temperature; \(d\), the characteristic depth; \(\alpha\), the thermal diffusivity of the fluid; \(k_L\) the water side mass transfer coefficient, and \(D\) is the diffusion coefficient of oxygen in the fluid.[25]

Equations. (1.12), (1.13), (1.14), and (1.15) are ‘water-side’ equations meaning that the variables pertain to the water side of the interface. This is because the resistance to oxygen transport is primarily on the water-side, as is demonstrated below. The Reynolds number uses \(U\) that is 5% of the wind speed, which is representative of the water current caused by wind shear[27].

Herein zero resistance to oxygen transport on the air-side of the air-water interface is assumed, resulting in the assumed concentration profile presented in Fig. 1.4 where the oxygen concentration profile is vertical on the air side and there is a finite concentration difference on the water-side. Since conservation of mass requires an equivalence for the mass flux on both sides of the interface, the air-side mass transfer coefficient must approach infinity, \(k_G \to \infty\). Although in this work \(k_G\) does not approach infinity, analysis of both \(k_G\) and \(k_L\) using classical laminar flat plate relationships shows that \(k_G \gg k_L\). The validity of the above assumption can be shown using a comparison of the predicted air- and water-side transport coefficients, \(k_G\) and \(k_L\), respectively, using a laminar flat plate boundary layer parameterization for \(Sh[4]\):

\[
Sh = 0.664 Re^{1/2} Sc^{1/3} \quad (1.16)
\]
Figure 1.4: Illustration of assumed concentration profile

where $Sc$ is the Schmidt number, and the water velocity is set to 5% of the air velocity.[27] This is a mass transfer boundary layer for the water-side of the system, as illustrated in Fig. 1.5. For the air-side, $k_G$ is obtained from the laminar unheated starting length solution for $Sh$[25]:

$$Sh_u = Sh_{|\xi=0} rac{L}{L - \xi} [1 - (\xi/L)^{3/4}]^{2/3}$$  \hspace{1cm} (1.17)

where $\xi$ is the “unheated length”, the length over which the velocity boundary layer develops, but where mass transfer is not occurring, as shown in Fig. 1.6; and $Sh_{|\xi=0}$, the Sherwood number for the case where the velocity and mass transfer boundary layers develop from the same starting point (Eq. (1.16)). Using Eqs. (1.16) and (1.17), values for $k_G$ and $k_L$ were obtained using the parameters presented in Table 1.1. The characteristic length used for $Re$ and $Sh$ was $L = 27.9$ cm which is the length of the experimental facility on the water-side. On the air-side of the experimental facility, $L = 114.9$ cm, and $\xi = 86.4$ cm. Using Eq. (1.16) to obtain $Sh$ on the water-side and Eq. (1.17) to obtain $Sh$ on the air-side and then obtaining the mass transfer coefficients gave $k_L = 8.8 \times 10^{-6}$ m/s and $k_G = 0.008$ m/s. Hence the air-side mass transfer coefficient is about three orders of magnitude
Figure 1.5: Illustration of water-side mass transfer boundary layer
Table 1.1: Parameters for Air-Side and Water-Side Mass Transfer Coefficient Comparison

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Air-Side</th>
<th>Water-Side</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wind Speed / (m/s)</td>
<td>4</td>
<td>0.2</td>
</tr>
<tr>
<td>$\nu$ / (m²/s)</td>
<td>$1.5 \times 10^{-5}$</td>
<td>$8.94 \times 10^{-7}$</td>
</tr>
<tr>
<td>$Sc$</td>
<td>0.75</td>
<td>356</td>
</tr>
<tr>
<td>$D$ / (m²/s)</td>
<td>$2.1 \times 10^{-5}$</td>
<td>$2.1 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

greater than that on the water-side, justifying the assumption described above.
Figure 1.6: Illustration of air-side velocity and mass transfer boundary layers
Chapter 2

Objectives

The goals of this experimental research are to:

• Parameterize $Sh$ as a function of $Ra$, $Re$, and $Sc$ for a range of $Ra$ and $Re$ that fall within mixed convection parameters

• Parameterize $Sh$ as a function of $Ra$, $Re$, and $Sc$ for a surfactant-covered surface and clean surface

• Compare the behavior of a water surface covered with oleyl alcohol to that covered with an indigenous surfactant under mixed convection conditions

• Correlate $Sh$ to $Re$ at low wind speed and $Ra \sim 0$ to draw conclusions about the impact of forced convection

• Correlate $\dot{m}''$ separately to $T_b - T_\infty$ and $T_b - T_s$ to draw conclusions about the behavior of gas exchange across a surfactant-covered surface and clean surface
Chapter 3

Experimental Method

3.1 Apparatus

Experiments were conducted in the wind/water tunnels illustrated in Figs. 3.1 and 3.2. The wind tunnel consists of a radial blower, diffuser, flow straightener, and test section. Two water tanks were used: one is 38.1 cm D × 27.9 cm L × 25.4 cm W (shown in Fig. 3.1), the other is 7.6 cm D × 27.9 cm L × 25.4 cm W (shown in Fig. 3.2), both are insulated with two layers of 1.9 cm thick polystyrene. In order to calculate an average surface temperature ($T_s$ in Eq. (1.14)), a ThermaCAM™ SC1000 infrared camera was used to capture the surface temperature field. A single value for $T_s$ was obtained from each image by averaging over all pixels, excluding those corresponding to the tank walls, bad pixels (described below), and the oxygen sensor or sensor wire (see Fig. 3.9, below). The surface temperature field captured by the infrared camera corresponds to an area on the water surface 20.3 cm × 20.3 cm in size, which is slightly smaller than the overall footprint of the water tanks. The infrared camera was mounted above the test section of the wind tunnel with the lens located 86.4 cm from the water surface and positioned 16° from vertical so the camera did not image a thermal reflection of itself. The water bulk oxygen concentration and temperature were measured using a Hach HQ30 oxygen sensor with an integrated thermistor. The sensor was positioned in the geometric center of the tank; it was assumed that the bulk water was well-mixed and therefore a single measurement was used to characterize the bulk temperature and oxygen concentration. The wire connecting the oxygen probe to the data logger hung in the middle of the test section of the wind tunnel. Examination of the infrared (IR) images attained from the IR
camera revealed no visible disruption of the surface flow due to the wire (e.g. Fig. 3.11). In order to keep a consistent surfactant coverage on the water surface, a reservoir and holder were constructed and placed in a corner of the tank. The reservoir was a \( \sim 4 \) cm long piece of Teflon tubing with a slit cut into it, as shown in Fig. 3.3. The holder was a piece of larger diameter tubing, such that the reservoir would fit into it snugly, secured to the tank by RTV silicone adhesive sealant \( \sim 2 \) cm below the top of the water tank. The location of the reservoir in the tank as well as the orientation of the slit is illustrated in Fig. 3.4. The surfactant reservoir and specifics of surfactant application are discussed in Section 3.2.

### 3.2 Experimental Procedure

Three surface conditions were explored, oleyl alcohol (controlled surfactant), tap (indigenous surfactant), and clean. A solution of oleyl alcohol and heptane was used on the surface of filtered tap water for the oleyl alcohol case. The heptane was used as a spreading agent for the oleyl alcohol.
Figure 3.2: Experimental apparatus showing wind/water tunnel with shelf tank and measuring equipment (not to scale)

Figure 3.3: Illustration of surfactant reservoir and slit
After being deposited on the water surface, the heptane evaporated, leaving only oleyl alcohol. The tap case was created by using filtered tap water without further cleaning. The clean surface case was created using tap water that was cleaned using a method described later in this section. Wind speeds from 0 - 4 m/s were investigated for the surfactant cases in increments of 1 m/s, and wind speeds of 1 - 4 m/s were investigated for the clean surface case, also in increments of 1 m/s. The reason for not including 0 m/s for the clean surface case will be explained later. The wind speed was characterized by an average of 9 wind speed measurements taken by a VelociCalc® Air Velocity Meter at locations uniformly spaced across the cross-section of the wind tunnel test section as shown in Fig. 3.5. Water that was heated to a temperature greater than that of the air was used to cause natural convection. Initial starting temperatures in the water bulk ranged from 30°C to 48°C for all surface conditions. These temperatures are all much warmer than the air temperature, normally around 23°C. Both hot tap water and/or an immersion heater were used to attain the desired starting temperature. For all experiments, once the starting temperature was attained, the water was allowed to cool naturally for the duration of the run. Clean surface runs were 15 minutes in duration, oleyl runs were 1 hour in duration, and tap runs were 8 hours in duration. The reason for the differences in durations is
One set of experiments investigated the impact of only forced convection. For these experiments, the tap case only was studied. Constant temperature water baths and wind were used to cool the water close to the equilibrium temperature to give $Ra \rightarrow 0$. The starting temperatures ranged from 14°C to 21°C, depending on ambient temperature, humidity, and wind speed. Like the experiments conducted for mixed convection conditions, once the experiment was started, only natural temperature change occurred.

Using the data collected in these experiments, $Sh$, $Ra$, $Re$, $Sc$, and $m''$ were calculated. In order to calculate $Sh$, the mass transfer coefficient must be calculated. The mass transfer coefficient is defined as:

$$k_L = \frac{\dot{m}}{A(C_A - C_W)}$$

where $C_W$ is the oxygen concentration in the water bulk; $C_A$, the concentration of oxygen in air (assumed to be constant for the duration of each experiment); $A$, the area of the water surface;
and $\dot{m}$, the mass transfer rate. The ratio of concentration of oxygen in the air, $C_A$, to the Henry’s Law constant, $H$, is equivalent to the concentration of oxygen on the water-side of the air-water interface $C_{W,i}$, i.e. $\frac{C_A}{H} = C_{W,i}$, which is assumed to be at solubility. The solubility data used to calculate $C_{W,i}$ (or $\frac{C_A}{H}$) was obtained from Tchobanoglous, et al.\cite{45} and varies with both temperature and barometric pressure. The barometric pressure data used to calculate $C_{W,i}$ was taken from the average pressure reported by the Clemson University Department of Entomology, Soils, and Plant Sciences for each day that an experiment was run, while the temperature data was taken from the average water surface temperature $T_s$. The mass transfer rate can be written as:

$$\frac{\dot{m}}{V} = \frac{d(C_A - C_W)}{dt} = k_L \frac{A}{V} \left( C_A - C_W \right)$$

(3.2)

where $V$ is the volume of water in the tank and $t$ is time. Hence, $k_L$ can be expressed as:

$$k_L = -\frac{V}{A} \frac{d(C_A - C_W)}{dt}$$

(3.3)

Separating variables, integrating, and reducing $\frac{V}{A}$ to $d$ gives:

$$\left( \frac{k_L}{d} \right) t = -\ln \left( \frac{C_A - C_W}{C_A - C_{W,0}} \right)$$

(3.4)

where $C_{W,0}$ is the initial oxygen concentration in the water bulk. If the mass transfer coefficient is a constant, then $(\frac{C_A}{H} - C_w)$ will decay exponentially resulting in a linear plot of $\ln(\frac{C_A}{H} - C_{W,0})$ versus time. A sample time-trace is presented in Fig. 3.6 showing linear behavior for $\ln(\frac{C_A}{H} - C_{W,0})$, and therefore constant $k_L$ for this particular run. For short runs in the deep tank, like those in Fig. 3.6, $k_L$ was computed by obtaining linear fits to the entire concentration time trace. This procedure was acceptable for the relatively short 15 minute clean surface runs, where the assumption of constant $k_L$ was appropriate. However, the oleyl alcohol and tap runs were 1 and 8 hours in duration, respectively, and hence the assumption of quasi-steady state was not valid. During this period of time, significant changes in the water temperature occurred, resulting in changes in $R_o$, and hence in $k_L$, invalidating the assumption that the decay in concentration is exponential. Likewise, the temperature decay in the clean surface runs in the shelf tank was too rapid to assume quasi-steady state. To address this, a sliding window of variable size was applied to the raw data for these runs that did not occur at quasi-steady state. Figure 3.7 is an example concentration time trace with
the window used to calculate \( k_L \) indicated. Each window was treated the same as the clean surface case described earlier, in that an exponential rise in \( C_W \) was assumed for the window. Each \( k_L \) was calculated by the slope of \( \ln\left(\frac{C_A - C_W}{C_A - C_{W,0}}\right) \) against time, as shown in Fig. 3.8, which is a plot of the data residing in the window indicated in Fig. 3.7. The large number of horizontal points in Fig. 3.8 are a result of the small rise in concentration for the window indicated in Fig. 3.7. The small concentration rise leads to digitization error becoming more apparent as compared to a window that has a larger rise in concentration, such as Fig. 3.6, where little, if any, digitization error is noticeable.

The window was slid over the entire \( C_W \) time trace, resulting in a value for \( k_L \) at each point in that time trace, excluding several at the beginning and end of the time trace where the window was too large for the available data. Because the temperature decreased continuously during the course of the experiment, some degree of error exists for any finite window size used since \( H \) varies with temperature. This error is quantified as:

\[
Z = \frac{k_1 - k_3}{k_C}
\]

where \( k_1 \) is the mass transfer coefficient computed with \( H \) evaluated at the maximum \( T_s \) in the window; \( k_3 \), the mass transfer coefficient with \( H \) evaluated at the minimum \( T_s \) in the window; and \( k_C \), the mass transfer coefficient with \( H \) evaluated at \( T_s \) in the center of the window. For each point in the time trace, the window size was iteratively adjusted until \( Z = 0.045 \), and then \( k_L \) was computed. This procedure insured that all values of \( k_L \) had the same (4.5%) error. This would not have been the case using a fixed window size, since the variation in \( T_s \) for a fixed sized window decreases as the rate of tank cooling decreases. The choice of \( Z = 0.045 \) was somewhat arbitrary; smaller values of \( Z \) yielded very noisy time traces of \( k_L \), and larger values of \( Z \) blurred the long time behavior of \( k_L \). Though a \( Z \) value was not imposed for the deep tank clean surface data, it was calculated for each experiment and varied from 0.96% to 9.1%.

The other dimensionless groups, \( Ra \), \( Re \), and \( Sc \) depend on the windows calculated above. Temperatures and temperature dependent properties are calculated using the value of the exponential fit to temperature at the middle of the window. For \( T_b \), \( \nu \), \( D \), and \( \frac{g\beta}{\nu} \), these fits are to bulk water temperature, while for \( T_s \), the fit is to water surface temperature.

Surface cleanliness was determined by examination of the IR images using the method described by Saylor[39] who showed that the presence of surfactant monolayers can be detected by
Figure 3.6: Time trace of log of concentration ratio for a clean surface run. The slope of this line is used to calculate $k_L$. 
Figure 3.7: Time trace of oxygen concentration for an oleyl alcohol run. The data in the window used to calculate $k_L$ is in between the dashed lines.
Figure 3.8: Time trace of log of concentration ratio for the window indicated in Fig. 3.7. The slope of this line is used to calculate $k_L$. 
the change in length scales observed in IR images. A sample IR image of a water surface covered
with oleyl alcohol is presented in Fig. 3.9, an image of a water surface covered with an indigenous
surfactant monolayer is shown in Fig. 3.10, and an image of a completely clean surface is presented
in Fig. 3.11. The clean surface is characterized by finer scale structures compared to the surfactant
surfaces. Some clean surface images, though, showed partial surfactant contamination, as seen
in Fig. 3.12. Indeed, Fig. 3.12 shows that a temperature difference exists between the clean and
surfactant-covered water surface. This difference was as much as 5°C. In all of the above images,
bad pixels can be observed (unresponsive pixels that appear black); however, these were not used
in calculation of $T_s$. The wire connecting the oxygen probe to the data logging unit (deep tank) or
part of the oxygen sensor itself (shelf tank) can be seen in all images; as noted above, this part of
the image was not used in calculation of $T_s$.

Uniform surfactant coverage was required for the oleyl alcohol experiments. In order to
create this, a $\sim 0.095$ M solution of oleyl alcohol in heptane was created. Heptane was used as a
spreading agent for the oleyl alcohol to ensure that the surfactant covered the entire water surface.
Initially, $\sim 55 \mu L$ of the oleyl alcohol solution was added to a reservoir on the water surface. This
amount of oleyl alcohol solution provided $\sim 10$ times the equilibrium spreading pressure of oleyl
alcohol as found by Vogel & Hirsa[47]. An amount 10 times greater than the equilibrium spreading
pressure was used so that the surfactant monolayer would remain even if surfactant loss occurred.
Additionally, 20 $\mu L$ of the surfactant solution was added every 20 minutes after the initial application,
to ensure complete surfactant coverage over the course of the experiment. The reservoir was used to
contain excess surfactant solution, as well as the heptane lens prior to its evaporation, on the water
surface to ensure uniform coverage on the water surface. As surfactant evaporated from the water
surface, surfactant seeped through the slit on the reservoir that was discussed in Section 3.1 (see
Fig. 3.3) keeping a consistent, uniform surface condition.

To create clean water surfaces, the method of Kou & Saylor[31] was used. Here the water
was first cleaned by bubble sparging, and then swiped with sterile tissue paper. However, removal
of surfactant was necessary throughout the experiment, since surfactant presumably originating
from both the water bulk and the air would build up over the course of a few minutes to form a
new monolayer. To remove this, a rake consisting of microbore tubes was precisely located at the
air-water interface, at the downstream end of the tank after swiping. Suction applied to the tube
rake from a peristaltic pump was used to remove surfactants from the water surface. This method
Figure 3.9: Surface temperature field of an oleyl alcohol covered water surface obtained from an IR image. The wind speed is $U=3$ m/s, and the wind direction is from bottom to top. The black line in the upper middle portion of the image is the oxygen sensor wire.

takes advantage of the tendency of the wind to blow surfactants to the downstream edge of the tank where the rake was located. Since wind stress was required for this apparatus to function well, 0 m/s experiments are not presented here for the clean surface condition. Indeed, as shown in Fig. 3.12, the water surface was not able to be completely cleaned at $U = 1$ m/s. A method for correcting this in the data processing is discussed in Section 3.3. The tap case was achieved by simply using tap water without any cleaning, since surfactants indigenous to tap water completely covered the water surface.

The oxygen concentration difference between the water and the air was created by sparging the water bulk with nitrogen for approximately 40 minutes before the beginning of each run. This oversaturation of nitrogen resulted in evacuation of oxygen from the water. Since the dissolved oxygen concentration within the water bulk was then below solubility, a concentration difference across the air-water interface existed to allow gas exchange. Once the experiments were initiated, oxygen was transferred from the air, assumed to be an infinite oxygen reservoir, to the water. Experimental
Figure 3.10: Surface temperature field of a tap water surface obtained from an IR image. The wind speed is $U=3$ m/s, and the wind direction is from bottom to top. The black line in the upper middle portion of the image is the oxygen sensor wire.
Figure 3.11: Surface temperature field of a clean water surface obtained from an IR image. The wind speed is $U=3 \text{ m/s}$, and the wind direction is from bottom to top. The black line in the upper middle portion of the image is the oxygen sensor wire.
Figure 3.12: Surface temperature field of a partially contaminated clean water surface obtained from an IR image. The wind speed is $U=1$ m/s, and the wind direction is from bottom to top. The black line in the upper middle portion of the image is the oxygen sensor wire.
runs were 1 hour in duration for the oleyl alcohol case, 8 hours for the tap case, and 15 minutes each for the clean surface case. Clean surface runs were shorter because the surfactant removal method described above no longer functioned properly when the water level fell beneath the tank rim which occurred after \( \sim 20 \) minutes of operation. Because the tube rake removed a small amount of water in the process of removing surfactants, the water surface was lowered and surface cleaning ceased after about 15 minutes, at which point data acquisition was stopped. For a typical tap run, the initial water temperature was \( 42^\circ C \). A typical clean surface or oleyl alcohol run began at a specified temperature, anywhere from \( 30^\circ C \) to \( 48^\circ C \). The 8 hour duration of the tap experiments allowed all runs to be started at the same temperature, since a satisfactory decrease in temperature occurred over that period. Oleyl alcohol runs were shorter due to the required periodic addition of oleyl alcohol on the water surface.

3.3 Image Processing

As discussed previously, partial surfactant contamination occurred at \( U = 1 \) m/s for the clean surface case. This is shown in the IR image presented in Fig. 3.12, where part of the surface is clean and part is covered by surfactant. This error can be accounted for by expressing the measured Sherwood number as:

\[
Sh_m = \alpha Sh_s + (1 - \alpha) Sh_c
\]  

(3.6)

where \( Sh_m \) is the partial contamination Sherwood number calculated from the raw data; \( \alpha \), the percentage surfactant coverage on the water surface; \( Sh_s \), the Sherwood number obtained from the power law fit to the oleyl alcohol data; and \( Sh_c \) the true Sherwood number for the clean surface. Rearranging, Eq. (3.6) gives:

\[
Sh_c = \frac{Sh_m - \alpha Sh_s}{1 - \alpha}
\]  

(3.7)

Digital image processing was used on these partially contaminated \( U = 1 \) m/s IR images to calculate \( \alpha \). These images were filtered by a two-dimensional fast Fourier transform (2D FFT) to eliminate small-scale structures in the clean surface that do not correspond to surfactant coverage then thresholded using an optimal thresholding algorithm to make each pixel correspond to one of
Figure 3.13: (a) Raw IR image of $U = 1$ m/s clean surface experiment (partial contamination) showing oxygen sensor, dead pixels, and tank edges. (b) Same image as in (a), but with adjacent pixels taking the place of oxygen sensor, dead pixels, and tank edges. (c) Image after asymmetric low-pass filtering by two-dimensional fast Fourier transform. (d) Image reconstructed after thresholding. Black indicates surfactant covered as well as wall and sensor pixels (not counted), while white indicates clean surface pixels.

two values: clean or surfactant. Since these images had large changes in intensity from the wire, tank edge, and dead pixels to the water surface, pixels adjacent to these areas were replicated as shown in Fig. 3.13(b) to attain better FFT performance. The image was also expanded from $238 \times 252$ pixels to $256 \times 256$ pixels for better FFT performance. This was again performed by pixel replication outward.

In order to eliminate small-scale clean surface structures (Fig. 3.13) so that they were not observed to be surfactant by the optimal thresholding algorithm, the FFT was filtered. Since these structures had a much higher frequency in the cross-stream direction as opposed to the downstream direction, where the surfactant coverage was most clearly defined, an asymmetric filter was applied to the 2D FFT, such that much more of the frequencies in the cross-stream direction were filtered out. All but the lowest 4 frequencies were filtered from the cross-stream direction while the lowest 106 frequencies remained in the streamwise direction from the $256 \times 256$ FFT. This FFT was then
inverted and cropped back to its original size, shown in Fig. 3.13(c), to be passed on to the optimal thresholding algorithm.

The filtered image (e.g., Fig. 3.13(c)) was sent to an iterative, optimal thresholding algorithm which is detailed in Sonka et al. [43] to determine two regions: surfactant-covered and clean surface. This algorithm was dependent on a histogram of the image. Prior to iteration, an initial guess of the threshold value \( \tau \) was made, which in this case was the mean intensity value of the image. At that point, two values were calculated, one for those below the threshold, assumed to be surfactant pixels:

\[
\mu_t^s = \frac{\sum_{(i,j) \in s} I N_s}{N_s}
\]

(3.8)

and another for those pixels above the threshold assumed to be clean:

\[
\mu_t^c = \frac{\sum_{(i,j) \in c} I N_c}{N_c}
\]

(3.9)

where \( s \) represents those pixels assumed to be surfactant covered, \( c \) represents the pixels assumed to be clean, \( i \) and \( j \) refer to the location of each pixel on the image, \( I \) is the intensity, \( N \) is the number of pixels at an intensity value \( I \), \( N_s \) is the total number of pixels below the threshold, and \( N_c \) is the total number of pixels above the threshold. These two values, \( \mu_t^s \) and \( \mu_t^c \), are used to calculate a new threshold:

\[
\tau^{t+1} = \frac{\mu_t^s + \mu_t^c}{2}
\]

(3.10)

This new \( \tau \) is then used to determine clean and surfactant pixels for Eqs. (3.8) & (3.9). This process is iterated until \( \tau^t = \tau^{t+1} + \epsilon \), where \( \epsilon \) is a convergence criteria, which is 1 in this work.

The histogram with the converged threshold obtained from the image in Fig. 3.13(c) can be seen in Fig. 3.14. The number of bins for each histogram were calculated using a method developed by Scott [42]:

\[
w = 3.49\sigma \frac{n^{1/3}}{n}
\]

(3.11)

where \( w \) is the bin size; \( \sigma \), the standard deviation of the intensities of the IR image; and \( n \), an arbitrary value, in this case chosen to be 100. The value for \( n \) is chosen to give the best balance
between retaining overall histogram shape and reducing noise in the histogram. Small values of $n$ resulting in a histogram that has a great deal of scatter from one bin to the next, while large values of $n$ result in the loss of large-scale histogram features, such as the secondary peak between 300-400 in Fig. 3.14, will not be retained.

Based on the number of pixels below and above the thresholding value, the percentage surfactant coverage $\alpha$ was calculated and used in Eq. (3.7) to obtain $Sh_c$, which is the Sherwood number presented in Section 4.1 for these $U = 1$ m/s clean runs. The IR image that was reconstructed after thresholding can be seen in Fig. 3.13(d). This image was not used for calculation, but for visual verification that the filtering and thresholding identified the proper area as being covered by surfactant.

### 3.4 Uncertainty Analysis

The uncertainty that exists in this system resulted primarily from the measurements of water bulk temperature ($T_b$), water bulk oxygen concentration ($C_W$), water surface temperature
Table 3.1: Uncertainty of Measuring Instruments

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Accuracy</th>
<th>(u_0) (zero-order uncertainty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(U)</td>
<td>±3%</td>
<td>±0.005 m/s</td>
</tr>
<tr>
<td>(C_W)</td>
<td>±0.1 mg/L</td>
<td>±0.005 mg/L</td>
</tr>
<tr>
<td>(T_b)</td>
<td>±0.3°C</td>
<td>±0.05°C</td>
</tr>
<tr>
<td>(T_s)</td>
<td>±2%</td>
<td>0.07°C (sensitivity)</td>
</tr>
<tr>
<td>(d &amp; L)</td>
<td>-</td>
<td>±0.025 cm</td>
</tr>
</tbody>
</table>

Table 3.2: Standard Deviation of Data from Fit

<table>
<thead>
<tr>
<th>Measurement</th>
<th>(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean Surface</td>
<td></td>
</tr>
<tr>
<td>(T_s)</td>
<td>0.0409°C</td>
</tr>
<tr>
<td>(T_b)</td>
<td>0.0429°C</td>
</tr>
<tr>
<td>(C_W)</td>
<td>0.0119 mg/L</td>
</tr>
<tr>
<td>Controlled Surfactant-Covered</td>
<td></td>
</tr>
<tr>
<td>(T_s)</td>
<td>0.0649°C</td>
</tr>
<tr>
<td>(T_b)</td>
<td>0.0310°C</td>
</tr>
<tr>
<td>(C_W)</td>
<td>0.00380 mg/L</td>
</tr>
<tr>
<td>Uncontrolled Surfactant-Covered</td>
<td></td>
</tr>
<tr>
<td>(T_s)</td>
<td>0.0500°C</td>
</tr>
<tr>
<td>(T_b)</td>
<td>0.0316°C</td>
</tr>
<tr>
<td>(C_W)</td>
<td>0.00380 mg/L</td>
</tr>
</tbody>
</table>

\((T_s)\), dimensions \((d \text{ and } L)\), and wind speed \((U)\). The goal of this uncertainty analysis is to find the uncertainty of the dimensionless groups: \(Sh, Ra, Re,\) and \(Sc\) for the three investigated conditions: clean surface, oleyl alcohol, and tap.

The accuracy and zero-order (resolution) uncertainty of the measurement instruments are shown in Table 3.1. The uncertainty in \(T_s\) presented in Table 3.1 uncertainty includes the in the black body source that was used to calibrate the IR camera that measured \(T_s\). This black body has a resolution of 0.1°C and accuracy of 0.2°C.

Many of these measurements are not used directly in the course of data processing. Instead, they are fit to a curve which is then used. For these terms, the standard deviation of the data from the fit is calculated and shown in Table 3.2.

These uncertainties are combined using the root of the sum of the squares:

\[
u_x = (u_0^2 + u_a^2 + \sigma^2)^{1/2}\]

(3.12)

where \(u_x\) is the combined uncertainty of a measurement \(x\); \(u_0\), the zero-order uncertainty; \(u_a\), the accuracy of the measurement; and \(\sigma\), the standard deviation of the data from the fit. For \(u_{T_b}\), the
uncertainties associated with the black body are included. The values of these total uncertainties are presented in Table 3.3.

How these individual measurement uncertainties propagate into the final dimensionless groups are calculated using the sequential perturbation method detailed in Figliola & Beasley[16]. In sequential perturbation, each uncertainty from Table 3.3 is applied by adding or subtracting the uncertainty value to/from the raw data value, which is then used in the data processing, for example with $Ra$ and $u_{T_s}$:

$$Ra_{T_s}^+ = f(T_s + u_{T_s}, T_b, d)$$

$$Ra_{T_s}^- = f(T_s - u_{T_s}, T_b, d)$$

where $Ra_{T_s}^+$ is the value of $Ra$ calculated with $T_s + u_{T_s}$ in place of $T_s$, while all other values remain unchanged from the calculation of $Ra$; similarly $Ra_{T_s}^-$ is the value of $Ra$ calculated with $T_s - u_{T_s}$ in place of $T_s$.

Defining $Ra_0$ as the value of $Ra$ without applying an uncertainty, two perturbations, $\delta Ra_{T_s}^+$ and $\delta Ra_{T_s}^-$, are calculated:
Table 3.4: Uncertainty for Each Dimensionless Group

<table>
<thead>
<tr>
<th>Dimensionless Group</th>
<th>Operating Point</th>
<th>Uncertainty</th>
<th>% Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean Surface</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Sh$</td>
<td>$6.42 \times 10^6$</td>
<td>$\pm 1.81 \times 10^4$</td>
<td>$\pm 2.83%$</td>
</tr>
<tr>
<td>$Ra$</td>
<td>$9.66 \times 10^6$</td>
<td>$\pm 5.21 \times 10^8$</td>
<td>$\pm 54.0%$</td>
</tr>
<tr>
<td>$Re$</td>
<td>$3.47 \times 10^4$</td>
<td>$\pm 575$</td>
<td>$\pm 1.66%$</td>
</tr>
<tr>
<td>$Sc$</td>
<td>$355$</td>
<td>$\pm 5.31$</td>
<td>$\pm 1.50%$</td>
</tr>
<tr>
<td>Oleyl Alcohol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Sh$</td>
<td>$6.24 \times 10^4$</td>
<td>$\pm 1.54 \times 10^5$</td>
<td>$\pm 2.47%$</td>
</tr>
<tr>
<td>$Ra$</td>
<td>$2.24 \times 10^7$</td>
<td>$\pm 5.69 \times 10^8$</td>
<td>$\pm 25.4%$</td>
</tr>
<tr>
<td>$Re$</td>
<td>$1.78 \times 10^4$</td>
<td>$\pm 553$</td>
<td>$\pm 3.11%$</td>
</tr>
<tr>
<td>$Sc$</td>
<td>$334$</td>
<td>$\pm 4.93$</td>
<td>$\pm 1.47%$</td>
</tr>
<tr>
<td>Tap</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Sh$</td>
<td>$7.93 \times 10^4$</td>
<td>$\pm 1.84 \times 10^5$</td>
<td>$\pm 2.23%$</td>
</tr>
<tr>
<td>$Ra$</td>
<td>$3.80 \times 10^9$</td>
<td>$\pm 6.41 \times 10^8$</td>
<td>$\pm 16.9%$</td>
</tr>
<tr>
<td>$Re$</td>
<td>$3.74 \times 10^4$</td>
<td>$\pm 613$</td>
<td>$\pm 1.64%$</td>
</tr>
<tr>
<td>$Sc$</td>
<td>$298$</td>
<td>$\pm 4.30$</td>
<td>$\pm 1.44%$</td>
</tr>
</tbody>
</table>

\[ \delta Ra_{T_s}^+ = Ra_{T_s}^+ - Ra_0 \]  
(3.15)

\[ \delta Ra_{T_s}^- = Ra_{T_s}^- - Ra_0 \]  
(3.16)

These terms are combined to give a total contribution from $T_s$:

\[ \delta Ra_{T_s} = \frac{\delta Ra_{T_s}^+ - \delta Ra_{T_s}^-}{2} \]  
(3.17)

where $\delta Ra_{T_s}^+$ and $\delta Ra_{T_s}^-$ always have of opposite signs in this work, meaning $\delta Ra_{T_s}$ can be considered the average of $\delta Ra_{T_s}^+$ and $\delta Ra_{T_s}^-$. The total uncertainty, then is the root of the sum of the squares combination of each contributing variable:

\[ u_{Ra} = \pm \left( (\delta Ra_{T_s})^2 + (\delta Ra_{T_s})^2 + (\delta Ra_d)^2 \right)^{1/2} \]  
(3.18)

The results of this uncertainty analysis are presented in Table 3.4, along with the operating points which were chosen near the middle of the data set. There is only one operating point for each case, i.e., all dimensionless groups are an ordered set.
Chapter 4

Results

4.1 Dimensionless Scaling $Sh \sim f(Ra, Re, Sc)$

A plot of $Sh$ versus $Ra$ is presented in Fig. 4.1 for the clean and oleyl alcohol runs under all wind speeds and tank sizes investigated. The deep tank data falls at a higher $Ra$ ($Ra > 10^9$) for both oleyl alcohol and clean surface cases compared to shelf tank data ($Ra < 10^8$). As was discussed in Section 3.3, the 1 m/s clean data was changed to account for partial surfactant contamination. The plot of $Sh$ against $Ra$ without this correction is presented in Fig. 4.2. The difference between these two plots is barely visible.

At a given $Ra$, the oleyl alcohol and clean surface data are separated by nearly an order of magnitude in Sherwood number. The oleyl alcohol data set appears to be well-fit by a single power law expressing $Sh$ in terms of $Ra$ without employing $Re$ or $Sc$, viz these gas exchange results show little dependence on wind speed. This power law fit was obtained by a linear fit to the $(\log(Ra), \log(Sh))$ data. The slope and intercept values of the fit correspond to the exponent and log of the pre-factor of the power law fit, respectively. The power law fit for the oleyl alcohol data is:

$$Sh = 86.6Ra^{0.310}$$ (4.1)

while the power law fit for the clean surface data is:

$$Sh = 1.50 \times 10^3 Ra^{0.316}$$ (4.2)
Figure 4.1: Sherwood-Rayleigh plot of clean surface (□ 1 m/s, △ 2 m/s, ○ 3 m/s, ◇ 4 m/s), and oleyl alcohol (♦ 0 m/s, ■ 1 m/s, ▲ 2 m/s, ● 3 m/s, ◀ 4 m/s), data and fits. For clarity, only every 10th shelf tank clean data point and every 20th oleyl alcohol data point are shown. All deep tank clean data points are shown.
Figure 4.2: Same data as Fig. 4.1, but clean $U = 1 \text{ m/s}$ data has not been corrected for partial surfactant contamination.
Figure 4.3: Semi-log Sherwood-Rayleigh plot of oleyl alcohol (♦ 0 m/s, ■ 1 m/s, ▲ 2 m/s, • 3 m/s, ◀ 4 m/s) data and fits. For clarity, every 20th data point is shown.

A small number of the oleyl alcohol data points for 0 m/s (located at $Ra \sim 10^9$) deviate significantly from the power law fit; these data points represent only 0.21% of the entire oleyl alcohol data set. These low values were likely due to small concentration rises through the course of the experiments. Small concentration rises led to larger digitization error, as evident in Fig. 3.8.

The lack of wind speed dependence of the oleyl alcohol data is further shown in Fig. 4.3, which is a semi-log Sherwood-Rayleigh plot of the oleyl alcohol data. While the deeper tank (higher $Ra$) data does not appear to collapse as well as it does in Fig. 4.1, the data also does not separate with wind speed.

Though the oleyl alcohol data does not appear to be dependent upon $Re$ or $Sc$, the RMS deviation of the data from the fit is used to verify this. The Sherwood number data from Fig. 4.1 is
scaled by $Re^n Sc^m$:

$$\frac{Sh}{Re^n Sc^m} \sim f(Ra) \quad (4.3)$$

where the exponents $m$ and $n$ are individually varied to find the set that corresponds to the minimum RMS deviation of the data from the fit.

Figure 4.4 presents an isocontour plot of the RMS of the data to the fit on $(m, n)$ coordinates. The data best collapses with an RMS of 0.0641 at $n = -0.1$ and $m = 0.09$. When $m$ and $n$ are 0, the RMS is 0.0820. This data does not take into consideration data at $Re = 0$. The impact of this weak $Re$ and $Sc$ dependence on the data can be seen in Fig. 4.5 below which is a plot of $Sh$ scaled by $Re^{-0.1} Sc^{0.09}$ versus $Ra$ for oleyl alcohol. This data looks very similar to the oleyl alcohol data in Fig. 4.1, showing the weak nature of the $Re$ and $Sc$ dependence for this surface condition. This power law fit for oleyl alcohol data is expressed as:

$$Sh = 118 Ra^{0.322} Re^{-0.1} Sc^{0.09} \quad (4.4)$$

The clean surface data, on the other hand, does not fit well to a single power law expressing $Sh$ only as a function of $Ra$. The clean surface data is plotted on semilog coordinates in Fig. 4.6 with power law fits applied by wind speed showing a slight wind speed dependence.

Figure 4.7 is an isocontour plot in $(m, n)$ coordinates of the RMS deviation of the clean surface data to a single power law fit, similar to Fig. 4.4 for oleyl alcohol data. Indeed, Fig. 4.7 shows that when $Sh$ is scaled by $Re^n Sc^m$, the data is better collapsed onto a single power law fit of $Ra$. The smallest RMS deviation is 0.208 at $n = 0.61$ and $m = 0.43$ as compared to an RMS deviation of 0.390 when $n$ and $m$ are 0, showing a numerically significant dependence of $Sh$ on $Re$ and $Sc$. A plot of $Sh$ scaled to $Re^{0.61} Sc^{0.43}$ for the clean surface data is presented in Fig. 4.8. The power law fit shown is:

$$Sh = 0.557 Ra^{0.263} Re^{0.61} Sc^{0.43} \quad (4.5)$$

Comparison of the oleyl alcohol data to the tap data can be seen in Fig. 4.9. This is data for the deep tank only, with the oleyl alcohol data corresponding to the high $Ra$ data shown in Fig. 4.1. Figure 4.9 shows that the tap water does not vary in behavior from the oleyl alcohol covered surface.
Figure 4.4: RMS deviation of oleyl alcohol data from the fit with changing $Re\,(n)$ and $Sc$ exponent ($m$).
Figure 4.5: Sherwood-Rayleigh plot of oleyl alcohol (■ 1 m/s, ▲ 2 m/s, ● 3 m/s, ◀ 4 m/s) data and fit scaled by $Re^{-0.1} Sc^{0.09}$. Every 20th data point is shown for clarity.
Figure 4.6: Semi-log Sherwood-Rayleigh plot of clean surface (□ 1 m/s, △ 2 m/s, ○ 3 m/s, ◄ 4 m/s) data and fits by wind speed. For clarity, every 10th shelf tank data point is shown. The fits increase with wind speed.
Figure 4.7: Contour plot showing the RMS deviation of the clean surface data from a single power law fit of $Ra$ for various combinations of $Re$ and $Sc$. 
Figure 4.8: Sherwood-Rayleigh plot of clean surface (□ 1 m/s, △ 2 m/s, ○ 3 m/s, ◀ 4 m/s) data, scaled by $Re^{0.61}Sc^{0.43}$. For clarity, every 10th shelf tank data point is shown.
Figure 4.9: Sherwood-Rayleigh plot of oleyl alcohol (♦ 0 m/s, ■ 1 m/s, ▲ 2 m/s, ● 3 m/s, ◀ 4 m/s) data and fit, tap (◇ 0 m/s, □ 1 m/s, △ 2 m/s, ◓ 3 m/s, ◇ 4 m/s) data and fit. For clarity, every 20th oleyl alcohol data point is shown and every 500th tap data point is shown.
4.2 Mass Flux and $\Delta T$

In applications, one is often more interested in actual mass fluxes and temperature differences, rather than the dimensionless groups, $Sh$, $Ra$, $Re$, and $Sc$. The two terms, $\dot{m}''$ and $\Delta T$ relate to the the mass transfer and overall driving force of heat transfer, respectively, in this system. To reveal trends in these terms, a plot is presented in Fig. 4.10 of the oxygen mass flux versus the bulk water to air temperature difference $T_b - T_\infty$. This plot shows that, for all wind speeds, the clean surface data gives significantly larger mass fluxes than its oleyl alcohol counterpart for a given $T_b - T_\infty$. There also appears to be a general trend of increasing mass flux with wind speed for the clean surface case, though there is no such behavior for the oleyl alcohol case, as presented in Fig. 4.11. These mass flux data are replotted in Fig. 4.12 in terms of oxygen mass flux versus the bulk to surface temperature difference $T_b - T_s$. This plot results in a partial collapse of the clean surface data set, not seen in Fig. 4.10. That is, when plotted in this way, the wind speed sensitivity for the clean-surface data is essentially eliminated. This plot also shows much larger mass fluxes for the clean surface case.

The range in $T_b - T_s$ is much larger for the oleyl alcohol case than for the clean case in Fig. 4.12 in spite of the fact that the range in $T_b - T_\infty$ for both cases is very similar, as shown in Fig. 4.10. This point is further explored in Fig. 4.13 where $T_b - T_s$ is plotted against $T_b - T_\infty$ for the clean surface and oleyl alcohol cases. The oleyl alcohol data show an increase in $T_b - T_s$ with $T_b - T_\infty$, particularly at the higher wind speeds that is not seen for the clean surface data. Also, $T_b - T_s$ increases with wind speed to a greater extent for the oleyl alcohol case than for the clean surface case. The $T_b - T_s$ data for the oleyl alcohol case in Fig. 4.13 show two groups of data for each wind speed, which is due to the different tanks used. This is most easily observed for the 4 m/s surfactant data, where a long “string” of data is a few tenths of a degree greater than the rest. This “string” of data is from the shelf tank, while the rest of the data is from the deep tank. The difference in temperature is likely due to the shelf tank cooling faster, meaning that the increased temperature difference corresponds to a faster response by the water bulk as compared to the deep tank. Overall, this plot reveals that the water surface is more effectively cooled by the wind when the surface is covered with a surfactant monolayer, and that without such a monolayer, increasing the wind speed does little to cool that surface. This point is explored in greater detail in the Discussion (Section 5).
Figure 4.10: Plot of mass flux of oxygen versus overall temperature difference ($T_b - T_\infty$) for clean surface (□ 1 m/s, △ 2 m/s, ◦ 3 m/s, ◀ 4 m/s) and oleyl alcohol (♦ 0 m/s, ■ 1 m/s, ▲ 2 m/s, ● 3 m/s, ◲ 4 m/s) data. For clarity, every 10th shelf tank clean data point and every 20th oleyl alcohol data point is shown.
Figure 4.11: Same data as in Fig. 4.10, but only oleyl alcohol (♦ 0 m/s, ■ 1 m/s, ▲ 2 m/s, • 3 m/s, ◄ 4 m/s) data presented. For clarity, every 20th oleyl alcohol data point is shown.
Figure 4.12: Plot of mass flux of oxygen and water side temperature difference ($T_b - T_s$) for clean (☐ 1 m/s △ 2 m/s, ○ 3 m/s, ◄ 4 m/s) and oleyl alcohol (♦ 0 m/s, ■ 1 m/s, ▲ 2 m/s, ● 3 m/s, ◀ 4 m/s) conditions. Every 10th shelf tank clean data point and every 20th oleyl alcohol data point is shown for clarity.
Figure 4.13: Plot of $T_b - T_s$ against $T_b - T_\infty$ for clean (□ 1 m/s, △ 2 m/s, ◆ 3 m/s, ◼ 4 m/s) and oleyl alcohol (♦ 0 m/s, ■ 1 m/s, ▲ 2 m/s, ● 3 m/s, ◄ 4 m/s) data. For clarity, every 10th shelf tank clean data point and every 20th oleyl alcohol data point is shown.
4.3  $Ra = 0$ Results

A plot of $Sh$ against $Re$ is presented in Fig. 4.14 for both tank sizes and all wind speeds investigated for the surfactant-covered case. These data points are taken at or as close to $Ra = 0$ as possible in order to show the impact of pure forced convection on gas exchange across the air-water interface. Attaining $Ra = 0$ conditions was challenging due to the fact that small changes in ambient temperature or relative humidity changed the equilibrium surface temperature. If the surface temperature decreased, natural convection (i.e., $Ra > 0$) would occur. This plot shows that there is very little change in $Sh$ with $Re$ at wind speeds below 4 m/s. $Re$ was calculated using water-side properties, including a characteristic velocity, $U$ that is 5% of the wind speed[27]. The shelf tank data is nearly one order of magnitude less than that of the deep tank data for a given $Re$. The value of $Sh$ for the surfactant data in the mixed and natural convection conditions presented earlier (Section 4.1) is higher than is seen for the pure forced convection case for each tank (Fig. 4.14).
Figure 4.14: Sherwood-Reynolds plot of indigenous surfactant deep tank (♦ 0 m/s, □ 1 m/s, △ 2 m/s, ◊ 3 m/s, ◊ 4 m/s) data and shelf tank (♦ 0 m/s, ■ 1 m/s, ▲ 2 m/s, ▼ 4 m/s) data. $Ra = 0$ for all data points.
Chapter 5

Discussion

The main result of these experiments can be seen in Fig. 4.1 which shows that the removal of a surfactant monolayer from a water surface results in about one order of magnitude increase in the Sherwood number for oxygen transfer, at a given value of $Ra$. This order of magnitude difference is significant compared to the uncertainty in $Sh$. Since $k_L$ is essentially the only variable in $Sh$ that changes in these experiments (Eq. (1.12)), this result shows that the presence of a surfactant significantly reduces the mass transfer coefficient. This point is revealed in a different way in Fig. 4.12, where the mass flux is shown to be dramatically reduced in the presence of a surfactant monolayer at any given value of $T_b - T_s$. The power law fits of $Sh$ to $Ra$ presented in Eqs. (4.1) & (4.2) for the oleyl alcohol and clean data sets, respectively, show that the surfactant reduces the overall magnitude of the gas exchange. Furthermore, as seen in Fig. 4.9, there is very little change, if any, for $Sh$ and $Ra$ when the surfactant is changed from the indigenous, naturally occurring surfactant in tap water to a controlled surfactant, in this case, oleyl alcohol.

The order of magnitude difference in $Sh$ between a surfactant-covered and clean water surface agrees with Asher & Pankow[2], who found that, at similar turbulence time scales, the mass transfer coefficient increased as much as nearly an order of magnitude from a surfactant covered surface to a clean water surface. McKenna & McGillis[35] found that surfactants reduced the mass transfer coefficient as much as a factor of four at high bulk turbulence $Re$. This trend is not consistent in both studies, which McKenna & McGillis[35] conclude is a result of the bulk turbulence not being characteristic of the turbulence at the air-water interface. Furthermore, Goldman et al.[21], found only a 50% reduction in $k_L$ for a surfactant covered surface. However, this study did not appear to
look at a rigorously cleaned water surface, as distilled water was used without further cleaning. As a result, this reduction may simply be as compared to a partially contaminated water surface. Hence, the present results are the first to show an order of magnitude difference in $Sh$, and thereby $k_L$, between a surfactant-covered surface and clean water surface during mixed convection conditions.

As noted in Section 1, the resistance to gas exchange exists almost exclusively on the water side of the air-water interface. Hence, transport will be determined by the degree to which the water-side turbulence reduces the boundary layer thickness. Indeed, this is shown by Fig. 4.1; for both clean surface and surfactant-covered cases, $Sh$ increases with $Ra$, which relates to the intensity of natural convection within the water, and thereby the amount of turbulence within the water bulk. Surfactant monolayers impart elasticity to the water surface, [1, 20] reducing the ability of subsurface motions to penetrate to the interface, thereby impeding transport. This mechanism is clearly in play in these experiments, where we see dramatic reductions in the Sherwood number and in the mass flux when a surfactant monolayer is present.

The analysis provided above does not, however, provide a complete picture of the transport processes. It is true that the elasticity of a monolayer can, and does, reduce transport. However, as shown in Fig. 4.13, for the surfactant case, $T_b - T_s$ is larger at a given value of $T_b$ (since $T_\infty$ is essentially constant, plotting $T_b - T_\infty$ instead of $T_b$ results only in a shift in the data) than for the clean case, and $T_b - T_s$ increases more with wind speed than for the clean case. Since $Ra$ is proportional to $T_b - T_s$ (Eq. (1.14)) this means that the presence of a surfactant increases the Rayleigh number (for a given $T_b$), and hence increases natural convection motion. It could be argued, therefore, that the presence of a monolayer, while reducing transport by suppressing turbulence near the interface, may also *increase* transport, by increasing the intensity of natural convection. Stated in another way, at a given value of $T_b$, and at a given wind speed, the deposition of a surfactant monolayer will serve to increase $T_b - T_s$ and $Ra$. This does indeed occur, however this effect is a minority player as can be seen in Fig. 4.1 which shows that for the entire range of $Ra$ explored here, the surfactant values of $Sh$ are much smaller than those for the clean case, even though the range in $T_b$ is about the same for these two cases. Hence, adding a surfactant will increase the natural convection, but this effect does not compete with the damping of subsurface turbulence that also occurs with the deposition of the monolayer.

Figures 4.1 and 4.5 also show that gas exchange shows little sensitivity to wind speed and thereby $Re$ when a surfactant monolayer is present, for the conditions explored here. This is not
surprising as the monolayer restricts motion at the air-water interface and, therefore, reduces the impact of forced convection induced by shear imposed on the air side of the interface. This is demonstrated more clearly in Fig. 4.14 where $Ra$, and therefore natural convection, is close to 0. There is some convective mixing within the tank under these conditions, though, as $Sh$ is 2 to 3 orders of magnitude larger than what it would be with only diffusion. The trends shown here that a general lack of wind speed sensitivity exists when a surfactant monolayer is present agrees with other research in which surface conditions are not taken into consideration, but an indigenous surfactant monolayer is likely present[9, 27, 34, 8, 7, 10, 37].

For the clean case, it is possible that the lack of surfactants lead to an increasing degree of mixing of the water and therefore gas exchange with wind speed. From Fig. 4.1, it is apparent that the single power law fit does not fit the clean surface data well. Indeed, the sets of data for the tanks appear to vary greatly in behavior not only from the single power law fit, but from each other as well. Evidence of this increase in mixing can be drawn from Fig. 4.13, where there is little change in $T_b - T_a$ for all wind speeds and $T_b$ as compared to the oleyl alcohol case, which has clear separation by wind speed. This separation points to the water surface being cooled by the wind as opposed to being mixed into the water bulk. As was discussed in Section 1.3, the elasticity of a surfactant monolayer makes it resistant to compression, whether this be from the air or water side of the interface[12]. Therefore, the monolayer will tend to resist wind shear, serving to hold the water surface in place, reducing the amount of mixing. However, the surfactant monolayer does not completely eliminate effects from wind shear, as seen by the slight dependence on $Re$ in Eq. (4.4). The wind speed sensitivity apparent in the clean surface data (Figs. 4.1 and 4.6) is resolved by the introduction of $Re$ and $Sc$ to the power law, as seen in Eq. (4.5) and Fig. 4.8. The difference in behavior of the two tanks discussed above appears to remain in Fig. 4.8, though. The apparent difference in behavior for the different tanks could be attributed to the large difference in surface area to depth. In the shelf tank, the large amount of surface area compared to the depth could mean that even at small $Ra$, parcels of water in the bulk reach the surface fairly quickly, so an increase in $Ra$ does not significantly decrease the amount of time for fluid parcels to reach the surface. This results in a weaker dependence of $Sh$ on $Ra$ compared to the deep tank. In the deep tank, the relatively small surface area compared to the depth leads to an increase in the amount of time parcels of water in the bulk take to reach the surface. At low $Ra$, parcels of water take significantly longer to reach the surface than at high $Ra$, which leads to $Sh$ having a greater dependence on $Ra$.
for the deep tank than the shelf tank. The uncertainty in $Ra$ reduces confidence in the wind speed dependence observed in the clean surface data (Figs. 4.1 and 4.8). However, other plots, such as Fig. 4.13, support the existence of a wind speed dependence for clean surface data.

The wind speed sensitivity difference between clean and surfactant covered water surfaces is the likely reason that the application of the percentage surfactant coverage (described in Section 3.3) does not appear to move the partially contaminated $U = 1 \text{ m/s}$ clean surface data from Fig. 4.2 in line with the rest of the $U = 1 \text{ m/s}$ clean surface data, as presented in Fig. 4.1. Since the presence of a surfactant tends to hold the water surface in place, wind shear is not able to effectively mix the surface water into the bulk as compared to a clean surface. As the partial contamination was amassed at the downstream end of the tank, as seen in Figs. 3.12 and 3.13, the water surface was separated into two coherent regions, clean surface (upstream) and surfactant contaminated (downstream). The characteristic length of the clean water surface, $L$, used in $Re$, therefore, should be shorter for these partially contaminated runs, encompassing only the clean portion of the water surface, instead of using both the clean and surfactant-covered parts. In terms of the data in Fig. 4.1, the partial surfactant contamination data points would have a lower $Re$ than those corresponding to a completely clean water surface. Therefore, these partial surfactant data points would act similar to those of a lower wind speed. Due to the relative wind speed sensitivity of the clean surface data to $Re$, this leads to the partially contaminated data sitting at a lower $Sh$ compared to completely clean $1 \text{ m/s}$ data.

There is also no noticeable difference in the behavior of the two kinds of surfactants studied, oleyl alcohol, the controlled surfactant, and the uncontrolled, indigenous surfactant in the filtered tap water. As the insoluble, liquid-phase surfactant monolayers explored here do not directly block gas exchange across the air-water interface\[12, 11, 19, 2, 32\], these two surfactants must reduce the subsurface turbulence by the same amount. Goldman et al.\[21\] concluded that the surface pressure of the surfactant monolayer, along with its solubility, determined the impact of the monolayer on gas exchange. However, Frew et al.\[19\] concluded that the elasticity of the surfactant monolayer explained the surfactant’s ability to damp gas exchange, which follows the analysis presented above for clean and oleyl alcohol surface conditions. Since both surfactants studied here had a similar effect on the gas exchange it is concluded that they had nearly the same elasticity.

This work seeks to parameterize the behavior of gas exchange for mixed convection conditions and both clean and surfactant-covered surface conditions. For nearly all water bodies, a
naturally occurring, indigenous surfactant exists\cite{35}, so the study of the impact of these surfactants is important. However, the importance of studying a clean water surface under these conditions is not as clear, especially as this condition was difficult to attain in a laboratory setting. In nature, a surfactant monolayer can be torn by wind stress and waves, among other things, leaving a clean water surface. Once the wind speed reduces or waves disappear, the monolayer does not instantaneously reconstitute\cite{21}, especially when a spreading agent is not present. Under these conditions, then, a clean water surface exists at low wind speeds. When an inland water body whose bulk water temperature is greater than that of the air, natural convection occurs. A common example would be that of a lake under low wind speeds at night in the summer, when the ambient temperature and radiation from the sun heats the water during the day, but once the sun sets and ambient temperature decreases below that of the water, mixed convection conditions occur. By combining these interfacial and convection examples, the applicability of this work becomes clear. Therefore, this work can be used to more completely describe the gas exchange for inland water bodies such as lakes, ponds, rivers, and reservoirs.

It is noted that these results were obtained for a fixed size water surface and a fixed upstream region over which the air-side boundary layer develops. Variation of these parameters could change the results obtained here.
Chapter 6

Conclusion

The effect of surfactants on gas exchange were observed under the condition of mixed convection. A parameterization of $Sh$ in terms of $Ra$, $Re$ and $Sc$ was obtained for surfactant-covered and clean surface conditions. However, for the surfactant conditions investigated here $Sh$ was found to be essentially insensitive to wind speed for both pure forced convection and mixed convection. The results showed that gas exchange is much more effective with a clean water surface than a surfactant covered one. The clean surface data also revealed much greater sensitivity of $Sh$ to $Re$ and $Sc$ than for the surfactant-covered case. Furthermore, the results showed that changing from a controlled surfactant (oleyl alcohol) to an indigenous one found in tap water has no observable impact on gas exchange. The cause for the differences between clean and surfactant covered results can be attributed to the elasticity imparted to the air-water interface by a surfactant monolayer. The similarity of the two surfactants studied was again concluded to be caused by similar elasticity of both monolayers. On the water-side of the interface, the surfactant reduces the subsurface turbulence, which in turn reduces mixing from the water surface to the bulk.
Bibliography


