

Sherwood–Rayleigh Parameterization for Evaporation in the Presence of Surfactant Monolayers

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*Presented here is an experimental investigation of the effects of several surfactant monolayers on evaporation driven by natural convection in the air above a water surface. Experiments were performed in a controlled laboratory setting with tanks of heated water for the following cases: (1) a clean water surface, and for surfaces covered with monolayers of (2) oleyl alcohol, (3) stearic acid, and (4) stearyl alcohol. Evaporation rates were measured using a laser-based method, and the Sherwood and Rayleigh numbers, Sh and Ra , were computed from the data. Power law scalings of the form $Sh = B \cdot Ra^m$ were developed for each case which yielded, essentially, $m = 1/3$ for all four surface conditions. The oleyl alcohol and stearic acid conditions give essentially the same value for B as for the clean surface case. For stearyl alcohol, B is smaller than for all other surface conditions; this result is attributed to the ability of the stearyl alcohol monolayer to inhibit evaporation by blocking the passage of water molecules through the monolayer: the barrier effect. The surface temperature is measured in this work enabling a separation of the effect of surfactants on evaporation due to a reduction in surface temperature from their effect on evaporation due to a true barrier effect. This has not been accomplished heretofore. © 2012 American Institute of Chemical Engineers *AIChE J*, 59: 303–315, 2013*

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Introduction

The evaporation of water is a transport process of importance to many fields including meteorology, limnology, oceanography, hydrology, and energy production. The ability to model and predict the evaporative losses from inland bodies of water is important for reasons related to the conservation and sustainability of fresh water.^{1,2} Evaporation is influenced by many factors³ including: temperature, pressure,⁴ wind^{5–7} and wind–wave interaction,⁸ salinity and ionic composition,⁹ and importantly the presence of surfactant monolayers^{4,10–13}; the latter is the focus of this research. The study of surfactant monolayers has long been related to the science of evaporation, and a host of investigations exist which quantify the ability of specific monolayers to inhibit evaporation rates.^{4,10–13} If it is desirable to retain and preserve fresh water supplies, then the application of evaporation inhibiting surfactant monolayers is a possible tool.^{10,14–16} Aside from the use of surfactant monolayers on fresh water reserves, researchers have investigated other means of reducing evaporation; one such study is that of Helfer et al.¹⁷ in which the seasonal temperature gradients in a large reservoir were artificially destratified with air-bubble plumes to decrease the surface temperature and thus reduce the evaporation rate. Hereforward, the focus of this article will remain on the effects of surfactant monolayers on evap-

oration. The equations developed from this research are fundamentally important and can facilitate the development of models used to predict evaporation from inland bodies of water.

The physical problem motivating the current work is that of evaporation from a heated water body. In this system, the bulk water temperature T_b and the surface temperature T_s are both greater than the temperature of the ambient air T_∞ . Such a physical scenario is common to industrial cooling impoundments and coolant reservoirs at power generation facilities, but can also occur in inland bodies of water when the air temperature drops below the water temperature during certain seasonal periods. In this scenario, natural convection occurs in the air above the relatively warm water surface, and drives the transport of water vapor into the ambient.

As outlined in Bower and Saylor,¹⁸ many studies seek to parameterize the net evaporative flux $\dot{m}''$ as

$$\dot{m}'' = f(\bar{u})(p_s - p_\infty) \quad (1)$$

where p_s and p_∞ are the water vapor pressures at the surface and in the ambient, respectively, and $f(\bar{u})$ is a function of the average wind speed $\bar{u}$. The wind speed function is often given by the form originally suggested by Penman¹⁹

$$f(\bar{u}) = a + b \cdot \bar{u} \quad (2)$$

where a and b are constants obtained from data. Sartori¹ provides a critical review of many equations having the form given in Eqs. 1 and 2 and shows disagreement in predicted $\dot{m}''$

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as large as 600% under certain conditions. The main problem with equations of the form presented in Eqs. 1 and 2 is that they do not take into account all of the relevant physics that drive evaporation: namely natural convection, the focus of this work. Under natural convection conditions, $\bar{u} = 0$ which, when substituted into Eqs. 1 and 2, results in an evaporative flux that is a linear function of the vapor pressure difference $\dot{m}'' = a \cdot (p_s - p_\infty)$, where a is a constant, which is to say that the mass transfer coefficient

$$h_m = \dot{m}'' / \Delta \rho_{wv} \quad (3)$$

becomes a constant ($h_m \propto a$). Here, $(p_s - p_\infty)$ is related to $\Delta \rho_{wv}$ (defined below) which is the the water vapor density difference between the immediate surface region and the ambient. A constant h_m for $\bar{u} = 0$ is physically incorrect, since an increase in the water-to-air temperature difference will result in an increase in the intensity of natural convection, thereby increasing h_m ; viz, h_m cannot be a constant. Thus, equations taking the form of Eqs. 1 and 2 cannot predict the physical behavior of natural convection-driven evaporation, which is a motivation for this study.

This research explores natural convection-driven evaporation via the relationship between the Sherwood number for evaporation and the Rayleigh number for air-side natural convection. Specifically, parameterizations are sought having the form

$$\text{Sh} = C \cdot \text{Sc}^x \text{Ra}^m \quad (4)$$

where Sc is the Schmidt number

$$\text{Sc} = \nu / \mathcal{D} \quad (5)$$

ν is the kinematic viscosity of air, and $\mathcal{D}$ is the diffusion coefficient of water vapor in air. The dimensionless mass transfer coefficient, Sh , is defined as

$$\text{Sh} = h_m W / \mathcal{D} \quad (6)$$

where W is the characteristic length of the system, herein defined as the horizontal dimension of the evaporating surface (the tank width). As noted above, h_m is defined in Eq. 3, and $\Delta \rho_{wv}$ is given by

$$\Delta \rho_{wv} = \rho_{wv}^{\text{sat}}(\bar{T}_s) - \phi \rho_{wv}^{\text{sat}}(T_\infty) \quad (7)$$

where $\rho_{wv}^{\text{sat}}(\bar{T}_s)$ and $\rho_{wv}^{\text{sat}}(T_\infty)$ are the saturation densities of water vapor evaluated at the water surface temperature $\bar{T}_s$ (averaged over the surface) and the ambient air temperature T_∞ , respectively, and ϕ is the relative humidity in the ambient. This density difference $\Delta \rho_{wv}$ serves as the driving potential for evaporation. The Rayleigh number Ra in Eq. 4 is defined as

$$\text{Ra} = \frac{g \Delta \rho W^3}{\bar{\rho} \nu \alpha} \quad (8)$$

where g is the gravitational acceleration, ν and α are the kinematic viscosity and thermal diffusivity of air, respectively, and $\Delta \rho$ is

$$\Delta \rho = \rho_\infty - \rho_s \quad (9)$$

where ρ_s and ρ_∞ are the densities of the air/water vapor mixtures at the water surface and in the ambient, respectively, and $\bar{\rho}$ is the average moist air density. In defining $\Delta \rho$, it is

assumed that the dry air and water vapor behave as independent, ideal gases at temperatures $\bar{T}_s$ at the surface and T_∞ in the ambient. The procedure for determining $\Delta \rho$ is presented by Sparrow et al.²⁰ and is also used in a previous paper by the authors.¹⁸ It is noted that $\Delta \rho$ is distinct from $\Delta \rho_{wv}$ in Eq. 7 as the latter quantifies the density of only the water vapor component of the moist air. As defined by Eq. 9, $\Delta \rho$ is a positive quantity throughout this experimental investigation. Thus, there exists a positively buoyant plume of moist air rising from the water surface into the cooler ambient.

Inclusion of Sc in the $\text{Sh} - \text{Ra}$ power law in Eq. 4 allows for the diffusive properties of the evaporating fluid to be taken into account. This becomes important when comparing the evaporative behavior of different fluids. In this study, the $\text{Sh} - \text{Ra}$ power law dependence on Sc is not considered because the focus is on water as the evaporant and Sc was practically constant throughout experiments: $0.57 < \text{Sc} < 0.58$. Thus, the $\text{Sh} - \text{Ra}$ power law given by Eq. 4 is rewritten

$$\text{Sh} = B \cdot \text{Ra}^m \quad (10)$$

where Sc has been absorbed into the coefficient B . This is the $\text{Sh} - \text{Ra}$ power law considered hereforward.

Few researchers have investigated the $\text{Sh} - \text{Ra}$ relationship for the evaporation of water under natural convection conditions. Sparrow et al.²¹ studied evaporation from circular pans ranging in diameter from 8.9 to 30.7 cm and chose the radius as the characteristic length. Unique to the work of Sparrow et al.²¹ was that T_b was less than T_∞ and so a buoyancy-driven downflow occurred from the room air to the water surface (i.e. Ra as defined by Eq. 8 was negative). This scenario is different from that considered here, but the $\text{Sh} - \text{Ra}$ results of Sparrow et al.²¹ are worth noting and are compared to those obtained herein.

Sharpley and Boelter²² and Boelter et al.²³ both studied the evaporation of heated water from a pan using a “quiet air apparatus.” This facility was a 5×5×7 foot chamber with baffles toward the top sides which acted to restrict the flow of air in the chamber. These authors noted that the presence of the baffles significantly changed the evaporation rates. Also, it is likely that the close proximity of the evaporation pan to the quieting chamber would have restricted the natural flow of air even further. On account of the experimental facility, the $\text{Sh} - \text{Ra}$ results from these two studies are therefore not likely to be representative of unrestricted natural convection conditions.

The three studies described earlier (Sparrow et al.,²¹ Sharpley and Boelter,²² and Boelter et al.²³) are the only known investigations (other than the authors’ previous work,¹⁸ described shortly) of the $\text{Sh} - \text{Ra}$ relationship for evaporation of water in air. None of these studies investigated the case of evaporation of heated water in a unrestricted natural convection scenario, which is a motivating factor for the present work.

In our previous work,¹⁸ a $\text{Sh} - \text{Ra}$ parameterization was obtained experimentally and compared with the prior work. During these experiments, warm untreated tap water was allowed to cool down in insulated tanks in a large laboratory environment while T_b , T_∞ , $\bar{T}_s$, ϕ , and $\dot{m}''$ were measured. Although no surfactants were ever directly applied, surfactant material was always naturally present over the entirety of the air/water interface as observed with an infrared (IR) camera. The quantity and composition of this indigenous surfactant material was unknown. To obtain $\dot{m}''$, a mass

Table 1. Comparison of Sh-Ra Power Law Coefficients and Exponents from Earlier Studies

Parameterization	B	m	Sc	Ra Range
Sh = $B Ra^m$				
Bower and Saylor ^{18,24}	0.263	0.306	0.57	$9.6 \times 10^5 < Ra < 5.7 \times 10^8$
Sharpley and Boelter ²²	0.891	0.213	0.57	$1 \times 10^6 < Ra < 4.5 \times 10^7$
Boelter et al. ²³	0.054	0.241	0.57	$9.3 \times 10^6 < Ra < 4.6 \times 10^8$
Sparrow et al. ²¹	0.645	0.205	0.57	$-6 \times 10^5 < Ra_L < -2 \times 10^4$
Goldstein et al. ²⁵	0.590	0.250	2.5	$2 \times 10^2 < Ra_L < 5 \times 10^3$
Lloyd and Moran ²⁶	0.169	0.327	2200	$8 \times 10^6 < Ra_L < 1.6 \times 10^9$
Lloyd and Moran ²⁶	0.50	0.255	2200	$2 \times 10^4 < Ra_L < 8 \times 10^6$

Lloyd and Moran,²⁶ Sparrow et al.,²¹ and Goldstein et al.²⁵ defined Ra according to Eq. 12, and the results of Sharpley and Boelter²² and Boelter et al.²³ have been recomputed from published experimental data to conform to Eq. 8. The water evaporation studies are given by Sc = 0.57.

balance was placed adjacent to the tank and held a small beaker of water on the weighing pan. A siphon tube connected the beaker to the water in the tank; thus, as water evaporated from the tank and the surface height changed, water would flow from the beaker to the tank through the siphon tube and the change in mass was constantly recorded. A correction to the equation used to compute $\dot{m}''$ is presented in an erratum,²⁴ and the resulting Sh – Ra power law is

$$\text{Sh} = 0.262 \text{ Ra}^{0.309}. \quad (11)$$

The goal of the previous work was to determine the Sh – Ra relationship for evaporation in the presence of natural convection above a heated water body. The study did not specifically investigate the effects of surfactants on evaporation. The absence of such a study is an important motivation for the present work. In the current investigation, the surface conditions are controlled, and a more direct and reliable method for the measurement of $\dot{m}''$ is used. This is the first time, to the authors knowledge, that the effects of surfactant monolayers on a clean surface have been studied to obtain a Sh – Ra relationship.

Two other studies were identified that investigate the Sh – Ra relationship for mass transport. However, these were not for evaporation. Goldstein et al.²⁵ investigated the sublimation of naphthalene from circular, square, and rectangular planforms. Because the planforms were solid, the boundary condition at the sublimating surface was of the no-slip type, which is different from the free surface conditions considered here. An important finding from the study was that the Sh – Ra data from all of the different geometries collapsed when a common length scale was used, the surface area to perimeter ratio $L^* = A/P$. Lloyd and Moran²⁶ studied the transport of copper ions (Cu^{2+}) from copper plates into a liquid solution (H_2SO_4 and CuSO_4) using an electrochemical method. The copper plates were circular, rectangular, square, and right triangular planforms, and L^* was also used as the length scale following the work of Goldstein et al.²⁵ Again, the boundary condition at the interface of the copper plates and liquid was of the no-slip type, and the relevant species of mass transfer are very different from the scenario of evaporating water.

The results of the aforementioned studies are summarized in Table 1. Several authors have defined Ra in a slightly different manner than considered above in Eq. 8. Lloyd and Moran,²⁶ Sparrow et al.,²¹ and Goldstein et al.²⁵ for example, defined the Rayleigh number as

$$\text{Ra}_L = \frac{g\Delta\rho L^3}{\bar{\rho}\nu D} = \frac{g\Delta\rho L^3}{\bar{\rho}\nu^2} \text{Sc} \quad (12)$$

where L is the characteristic length. This definition presumes that the buoyancy is dissipated by viscous diffusion and the

diffusion of mass, the latter indicating that the smearing of the water vapor concentration gradient due to $\mathcal{D}$ has an adverse effect on $\Delta\rho/\bar{\rho}$. This is clearly not the case in the present work, where the buoyancy is dissipated by thermal and viscous diffusion (and the concentration of water vapor has an essentially negligible effect in $\Delta\rho/\bar{\rho}$); for this reason, Eq. 8 is used here instead of Eq. 12. Furthermore, Sharpley and Boelter²² and Boelter et al.²³ used an alternative definition of Ra, and tabulated their raw experimental data in their publications; this allowed the data to be recomputed according to the definition in Eq. 8 for comparison with the present results.

Clearly, the number of studies of mass transfer in the presence of natural convection is quite limited; of the investigations listed in Table 1, only three have studied the evaporation of water. Particularly important is that none of these studies have investigated how surfactants affect the Sh – Ra parameterization, making the present study especially relevant.

Whereas there has been no quantification of the effect of surfactants on the Sh – Ra parameterization in particular, the effect of surfactants on evaporation in general has a rich literature.^{10,11,13,15,16,27–52} In this literature, evaporation is usually studied in a Langmuir trough apparatus where the evaporation rate is measured with and without the presence of a certain surfactant monolayer. The effect of the monolayer on evaporation is then quantified via a monolayer resistance r_m (e.g., Barnes⁵³)

$$r_m = \Delta\rho_{\text{wv}} \left(\frac{1}{\dot{m}''} - \frac{1}{\dot{m}''_o} \right) \quad (13)$$

where $\dot{m}''_o$ is the evaporative flux from a clean surface, and $\dot{m}''$ is the evaporative flux from the surfactant covered surface. Note that, invoking Eq. 3, r_m is simply the difference between the inverse of the mass transfer coefficients for clean and surfactant covered surfaces.

Surfactant monolayers can reduce the evaporation rate via two mechanisms. The first is by a reduction in surface temperature that occurs because of the elasticity of the monolayer which serves to restrict motion at the interface when convective transport is occurring in the water bulk. In so doing, the water which is cooled via evaporation resides at the surface for a longer period of time, resulting in a lower $\bar{T}_s$. The elasticity also reduces $\bar{T}_s$ by inhibiting convective transport of heat within the water.^{43,54} This reduction in $\bar{T}_s$ in turn results in a lower value for $\rho_{\text{wv}}^{\text{sat}}$ at the surface and, according to Eq. 7, a smaller driving force for evaporation. The second way in which a monolayer can reduce evaporation is via a barrier effect, wherein the ability of water molecules to move from the water surface into the air is restricted

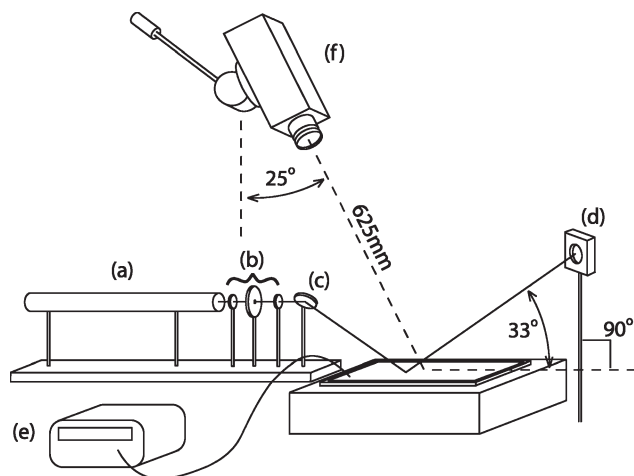


Figure 1. The experimental facility consisting of an insulated water tank and (a) laser, (b) spatial filter components, (c) mirror, (d) PSD, (e) temperature data logger with the T_b probe inserted into the water tank, and (f) tripod-mounted IR camera.

The T_∞ and ϕ probes are not shown here since they are located far from the tank.

by the presence of the monolayer. This barrier effect is theorized to be due to the activation energy barrier of the film,^{30,31,55} the reduction in accessible surface area through which water vapor can pass when monolayer molecules are assumed to be impermeable,^{40,41,53} or the probability of accessible hole formation in the monolayer film.^{52,56} In the evaporation suppression literature, $\Delta\rho_{wv}$ used in computing r_m is not evaluated according to Eq. 7 where the density of water vapor at the water surface is evaluated at the average surface temperature $\bar{T}_s$. Rather, the density of water vapor at the surface is evaluated using the bulk water temperature T_b , or by estimating the surface temperature using measurements of T_b . This is a critical difference from the approach used herein. By evaluating the water vapor density at the surface using T_b , prior studies combine both of the mechanisms described earlier by which surfactants can reduce evaporation into r_m . Accordingly, the degree to which one or the other of these mechanisms is contributing to evaporative suppression cannot be separated out.

In the extant literature, there has been a general recognition that monolayers can affect the surface temperature; for example, Jarvis and coworkers have looked at this.^{57–59} However, it is not clear if prior researchers truly appreciated the necessity of measuring T_s during evaporation experiments or when attempting to determine the pure barrier effect of a monolayer. In some cases, it seems that researchers chose to assume that T_b and T_s were either equal or very similar in magnitude,^{7,13,21–23} or developed experimental apparatus designed to make T_b and T_s very similar.^{11,38,48,60,61} Other researchers attempted to extrapolate T_s from measurements obtained close to the surface and in the bulk over a range of depths.^{42,43,62} Many researchers regard T_s as the temperature measured by a probe positioned barely below the surface. However, even for very small probes, this method can induce surface flows, causing inaccuracies in the measurement.

An important goal of the present work is to ascertain the resistance due solely to the barrier effect. Accordingly, $\bar{T}_s$ is

measured accurately using an IR camera, and ρ_{wv}^{sat} at the surface is computed using the saturation value at $\bar{T}_s$. When done in this way, a monolayer that only reduces evaporation via depression of the surface temperature will have no effect on either r_m or Sh, providing a unique, definitive method for ascertaining precisely how a monolayer affects evaporation. Stated another way, what we wish to know is, at a fixed $\bar{T}_s$, T_∞ , and ϕ , does a monolayer reduce $\dot{m}''$? If the answer is yes, then such a monolayer provides a physical barrier to evaporation, reducing evaporation in a way that is very different from the effect due to a simple reduction in $\bar{T}_s$. Whether or not this is the case is determined herein via the Sh – Ra parameterization, and has not been determined heretofore.

Experimental Method

The apparatus used for these experiments is shown in Figure 1. During the course of each experimental run, an insulated glass tank was filled with distilled water and allowed to cool from approximately 44–33°C over the course of roughly one hour. In this scenario, natural convection occurred both in the air and in the water bulk due to temperature (and thus buoyancy) gradients. Measurements of $\dot{m}''$, T_b , $\bar{T}_s$, T_∞ , and ϕ were collected during each of these cool-down experiments. From these measurements, Sh and Ra were subsequently computed. The surface conditions were imposed by applying surfactant monolayers of (1) oleyl alcohol, (2) stearic acid, and (3) stearyl alcohol, and by removing all indigenous surfactant material to obtain (4) a clean surface.

Experiments were conducted using a total of seven insulated glass tanks, each square in footprint. The dimensions of all seven tanks are presented in Table 2. As shown in Eq. 8, Ra scales with the tank width W raised to the third power. Accordingly, varying W is an effective way to explore a large range in Ra, and here four different W were used giving a range in Ra over all experiments of $3 \times 10^6 < \text{Ra} < 5 \times 10^8$. Four different tank depths D were also used for the $W = 30.4$ cm tank to vary the water-side Rayleigh number for a concurrent Nusselt–Rayleigh convective heat transfer investigation.⁵⁴ The range of D does not have a measurable effect on the behavior of the air flow above the surface, but these data are included here simply to increase the total data available. For each tank listed in Table 2, at least twelve clean surface runs were conducted and at least three runs were conducted in each tank for each of the three surfactant monolayers considered. In total, 63 surfactant runs and 103 clean surface runs are reported here.

Before each experiment, a careful and regular cleaning procedure was performed on all wetted components of the experimental setup. This was done to minimize water contamination due to dust and residual surfactant material. The tank and T_b probe were rinsed with distilled water and wiped

Table 2. A Summary of the Different Tank Sizes Used During Experiments (Indicated with X)

		W			
		15.2(cm)	30.4(cm)	45.6(cm)	60.8(cm)
D	5.0(cm)	X	X	X	X
	10.1(cm)	–	X	–	–
	15.2(cm)	–	X	–	–
	35.5(cm)	–	X	–	–

The tanks are square in footprint.

thoroughly with Kimwipe-brand tissues and reagent grade methanol (>99%, Sigma-Aldrich). The distilled water was heated in the tank to roughly 44°C using an immersion heater. The surface was then cleaned by sweeping a Kimwipe tissue across the interface to remove indigenous surfactant material. Use of the IR camera allowed the surface cleanliness to be visually monitored,⁶³ and the sweeping procedure was repeated until the surface was entirely clean. Once the surface was determined to be free of indigenous surfactant material, either the surface was prepared with one of the surfactant monolayers or a clean surface experiment was initiated.

All surfactant monolayers used here are insoluble in water, and none of the films were physically compressed. The compression of a monolayer is quantified by the surface pressure, π , defined as

$$\pi = \sigma_0 - \sigma \quad (14)$$

where σ_0 is the surface tension of the surface when it is clean, and σ is the surface tension in the presence of the monolayer. More surfactant material was applied than was needed to form a monolayer in these experiments. Under these conditions, π is equal to the equilibrium spreading pressure π_{esp} of each film. Because an excess amount of material was present, sufficient surface coverage was guaranteed; that is, depletion of the film due to evaporation or dissolution into the bulk would not result in a deviation from π_{esp} because surfactant would self-spread from the excess.^{10,64}

The same procedures were used to apply these surfactants as described by Bower and Saylor.⁵⁴ Oleyl alcohol ($\text{C}_{18}\text{H}_{36}\text{O}$, purity >99%, Sigma-Aldrich) was applied to the surface with a microsyringe in a 50.0 mg/mL solution of heptane (HPLC grade purity >99%), which aided with spreading. The quantity of oleyl alcohol applied was approximately 10 times the amount required to reach π_{esp} . Stearic acid ($\text{C}_{18}\text{H}_{36}\text{O}_2$, also octadecanoic acid, purity >98%, Sigma-Aldrich) was applied to the surface in a 1.4 mg/mL solution of heptane⁶⁵ which was approximately ten times the amount required to reach π_{esp} . Finally, solid flakes of stearyl alcohol ($\text{C}_{18}\text{H}_{37}\text{OH}$, also octadecanol, 95% purity, Acros Organics) were finely ground into a powder and evenly distributed at the surface at an area concentration of roughly 1.3 g/m². Some solid particles of stearyl alcohol remained undepleted at the interface after the monolayer spread from the flakes and were visible to the naked eye. For all three surfactants, the films were allowed to equilibrate on the surface for no less than 5 min before beginning an experiment. The thickness of a monolayer at a surface is related to the chain length of the molecule. Here, all three surfactants have the same number of carbons atoms in the chain structures, and thus, the surfactant molecules are all approximately 2.1 nm in length; this value is the maximum possible monolayer thickness when the molecules are oriented normal to the surface.

The three surfactants used here were selected based on how they affect evaporation. Oleyl alcohol is thought to not measurably inhibit evaporation.¹² Stearic acid has been shown to inhibit the evaporation rate, but only when physically compressed with a movable barrier beyond π_{esp} , which was not the case here. Importantly, stearyl alcohol has been shown to inhibit evaporation at π_{esp} when spread according to the procedure described earlier.^{11,16}

The clean surface runs were typically conducted with T_b a few degrees warmer than for the surfactant runs which

helped maintain surface cleanliness. After the warm, distilled water was swept free of indigenous surfactant material as previously discussed, the experiment was initiated. After 5–10 minutes, indigenous film material would begin to accumulate at the surface, typically in the tank corners. This surfactant material is presumed to come from either particles in the air or the wetted tank walls in spite of the described cleaning procedure. A second IR camera (not shown in Figure 1) was used to observe the entire tank surface. As IR images can be used to ascertain surface cleanliness,⁶³ the images from this camera were used to ascertain when contamination began, at which time data-taking for the clean surface run was terminated. The water surface was then cleaned once again to begin a new clean surface run.

IR imagery of the surface temperature field was acquired at a rate of 3 Hz using an M-Wave IR camera. The InSb focal plane array (320×240) was sensitive to light in the 1.5–5.5 μm wavelength band for which the effective optical depth of water is approximately 40 μm ⁶⁶; beyond this depth, liquid water is opaque. The camera was fixed 25° from vertical with a 625 mm distance separating the lens from the water surface. This resulted in an imaged water surface area of roughly 7.6 × 5.7 cm with a resolution of 42 pixels/cm. The camera was calibrated to an accuracy of ±0.082 K according to the procedure developed by Bower et al.¹⁸ before experiments. The mean surface temperature $\bar{T}_s$ was determined for each image from the instantaneous spatial average of all 76,800 pixels in the image.

A laser-based method was used to measure $\dot{m}''$ by measuring the rate of change of the height of the water surface. The main components of the laser apparatus are shown in Figure 1 and include a HeNe laser (10 mW JDS Uniphase Model 1135), a spatial beam filter (two lenses and a pinhole aperture), a tilted mirror, a position sensing detector (PSD), a signal amplifier, and a data acquisition device. All components of the laser setup were fixed securely to an optics bench. To reduce the effect of any building vibrations, the optics table was mounted atop four rubber inner tubes (≈25 cm diameter) inflated to ≈3 psi. All four tubes were connected to each other so that they were at the same pressure. A small bag of sand was placed within the center of each tube. The laser beam (0.68 mm diameter) was passed through a spatial filter to create a Gaussian beam profile. A mirror was used to direct the beam down toward the water surface at an angle of approximately 57° from normal. A component of this beam was reflected off of the water surface and was collected by the PSD (On-Trak PSM2-20 Duo-lateral PSD Module with a silicon photodiode detector). The PSD was mounted so that its normal was parallel to the water surface; in this geometry, a change in the vertical position of the beam on the PSD of h corresponded to a change in the water surface height of $h/2$. This relationship was independent of the angle at which the beam was directed toward the tank surface, and 57° was used here to accommodate the physical dimensions of the experimental facility. The PSD amplifier (On-Trak OT-301) provided two analog outputs (±10V) which correspond to the horizontal and vertical location (or x and y location, respectively) of the centroid of the light striking the PSD surface. The intensity of the laser was large enough that the contribution of ambient light from the laboratory to the PSD outputs was negligible. The y -axis signal, Y , was acquired with a DATAQ DI-158U A/D converter at a rate of 80 Hz; the horizontal position of the laser was essentially constant, and

thus, the x -axis signal was ignored. Changes in the height of the surface were measurable to within $5\ \mu\text{m}$. This $5\ \mu\text{m}$ limit was due to amplifier noise. During a typical experiment, the height of the water surface would decrease by approximately $0.4\ \text{mm}$. The fluid depth D used in Ra in Eq. 8 was regarded as a constant, however, as shown in Table 2.

A calibration was performed with the PSD to determine the physical location of the beam on the y -axis from Y by attaching the PSD to a vertical micrometer stand ($10\ \mu\text{m}$ resolution). The laser was directed onto the PSD and Y was recorded for PSD positions over a $2\ \text{mm}$ range, giving a calibration coefficient $C = 992.2 \pm 7.9\ \text{mV/mm}$. The ability of the laser setup to accurately measure $\dot{m}''$ was further tested in separate experiments by adding room temperature water into a tank at a known, steady rate with a programmable syringe pump while the laser system recorded the changing height of the surface. A range of $50\ \text{mg}/(\text{m}^2 \cdot \text{s}) < \dot{m}'' < 450\ \text{mg}/(\text{m}^2 \cdot \text{s})$ was tested which covered the range of $\dot{m}''$ expected during the experiments. The laser setup was able to measure $\dot{m}''$ to an uncertainty of $\pm 9.1\ \text{mg}/(\text{m}^2 \cdot \text{s})$ of the mass flux provided by the syringe pump.

It is important to note that the height of the water surface decreased on account of both evaporative loss and volumetric (i.e., density) change due to cooling of the liquid water. Accordingly, the net evaporative flux was

$$\dot{m}'' = -\rho \left(\frac{C}{2} \frac{dY}{dt} - \beta D \frac{dT_b}{dt} \right) \quad (15)$$

where C is the position-to-volts conversion from the PSD calibration, and β is the volumetric expansivity of water. The first group of terms within the parentheses in Eq. 15 represents the measured height change of the water surface, and the second group of terms is the correction for the density change of the liquid water from cooling. Values for h_m and Sh were subsequently computed from $\dot{m}''$ using Eqs. 3 and 6, respectively.

Equation 15 requires time derivatives of Y and T_b , which were obtained by first fitting these data to an equation and then obtaining the derivative analytically. Different fits were used depending on whether the surface was clean or covered with surfactants. The T_b data for the surfactant runs were fitted with an exponential function of the form

$$T(t) = (T_i - T_a)e^{-t/\tau} + T_a \quad (16)$$

where T_i , T_a , and τ are the initial temperature, asymptotic temperature (i.e., T as $t \rightarrow \infty$), and the temperature decay time constant, respectively. The standard deviation of the T_b data from the fit given by Eq. 16 was $S_{T_b} = 0.02^\circ\text{C}$. The exponential form given by Eq. 16 was also used to fit $\bar{T}_s$. The standard deviation of the $\bar{T}_s$ data from the fit was $S_{\bar{T}_s} = 0.05^\circ\text{C}$. The time derivative of T_b is obtained analytically and is

$$\frac{dT_b(t)}{dt} = -\frac{1}{\tau} (T_{b,i} - T_{b,a}) e^{-t/\tau} \quad (17)$$

The PSD signal Y was fit using Eq. 16 as well, with fitting parameters Y_i , Y_a , and τ which are the initial value $Y(t=0)$, the asymptotic value of Y as $t \rightarrow \infty$, and the PSD signal decay time constant, respectively; dY/dt was computed analytically (similar to Eq. 17 for the T_b data).

For the clean surface data, T_b , $\bar{T}_s$, and Y were all fit to a straight line due to the relatively short duration of these

runs. Thus, each fit to T_b and Y gives a single value for the time derivatives which were used to compute $\dot{m}''$ in Eq. 15. As a result of this, data from each clean surface run are indicated by a single point when plotted.

The Schmidt number for water vapor in air is essentially constant at $Sc = 0.58$ throughout these experiments. The fluid properties, ν , α , and μ were evaluated at a temperature equal to the average of $\bar{T}_s$ and T_∞ , and D was evaluated according to:⁶⁷

$$D = D_{298\text{ K}} \left(\frac{\bar{T}_s + 273}{298\text{ K}} \right)^{3/2} \quad (18)$$

where $D_{298\text{ K}}$ is the diffusion coefficient of water vapor in air at 298 K , and $\bar{T}_s$ is in units of $^\circ\text{C}$.

Results

Sample IR images of the different surface conditions are shown in Figure 2. The IR image intensity corresponds to temperature; light pixels indicate warm regions, and darker pixels indicate cooler surface regions. Present in these images are long, slender dark lines, or sheets (longer in the surfactant images than in the clean ones). These sheets are indicative of the temperature nonuniformity and the motion in the underlying water bulk as the water undergoes natural convection; the regions between the sheets show where the warm, buoyant fluid is upwelling from the bulk. At the surface, the fluid collects in the sheet regions as evaporative cooling occurs before subsequently plunging back down through the bulk. Throughout the course of an experiment, these sheets wander about the surface.

Figure 2a reveals the fine scale structures that are characteristic of the clean surface condition. Several small islands of indigenous surfactant material exist on the clean surface in Figure 2a. As shown by Saylor,⁶³ comparing the surfactant images in Figures 2b–d with the clean surface image in Figure 2(a) shows that the use of the IR camera allows for the clean surface condition to be easily distinguished. When oleyl alcohol, stearic acid, or stearyl alcohol are present, the fine scale structures disappear and dark, slender sheet regions emerge. Furthermore, observed in real time, the motion at the surface is much slower for the surfactant case than for the clean surface case.

A typical time trace of the changing height of the water surface is presented in Figure 3 along with a curve fit having the form presented in Eq. 16. The surface height is related to Y through the calibration constant, C . It is apparent in Figure 3 that the magnitude of the noise in the PSD measurements is relatively large. This noise is due to small scale water waves caused by building vibrations which existed in spite of the vibration-damping precautions described earlier. The time scale of these waves were very small compared to the time scale of evaporation. Additionally, because these waves were very small in amplitude, they were sinusoidal, meaning that the average position was not affected. The inset in Figure 3 shows the probability density function of the deviations of the surface height from the fit to the surface height; the PDF is highly Gaussian (represented by the solid line superimposed on the PDF). This indicates that the fit well-represents the time-averaged change in the height of the water surface despite the noise from the surface waves. The PSD signal was processed to remove the frequency content of the noise $> 10\text{ Hz}$ with a 10th order Butterworth

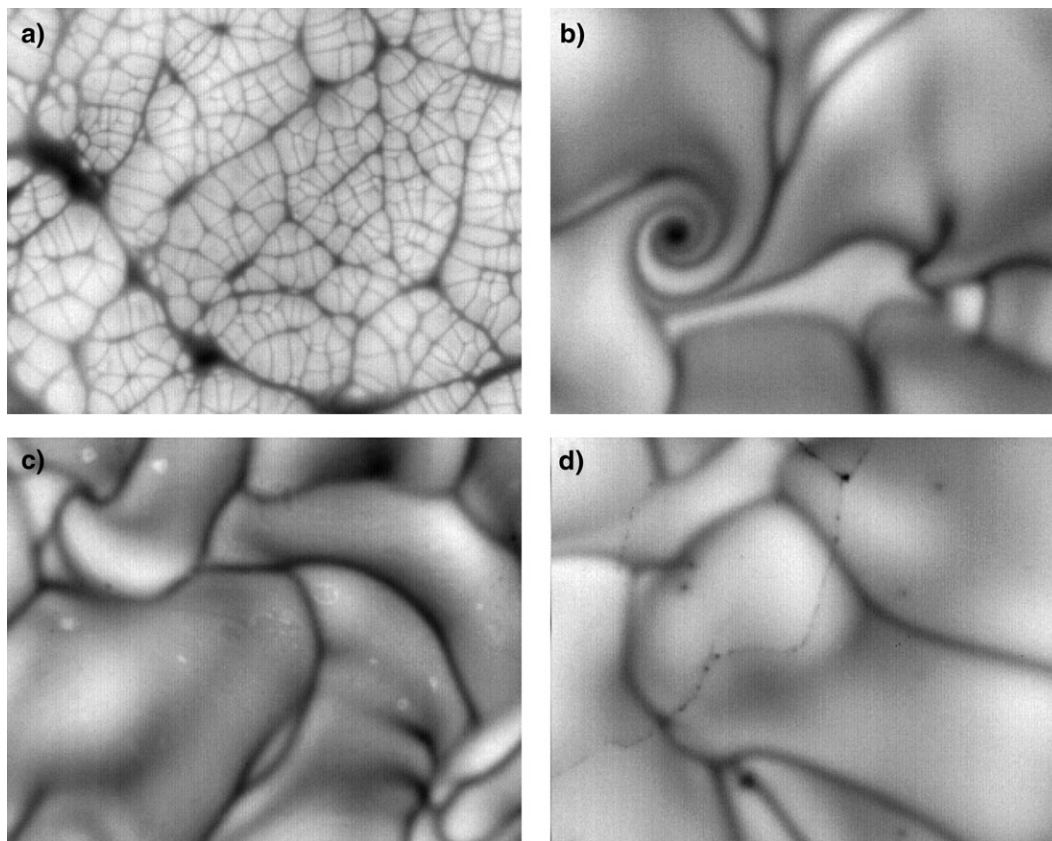


Figure 2. IR images from experiments with: (a) a clean water surface, (b) an oleyl alcohol covered surface, (c) a stearic acid covered surface, and (d) a stearyl alcohol covered surface.

For all images, the temperature of the underlying water is $T_b \approx 35^\circ\text{C}$. The observed surface region is approximately $7.6 \times 5.7 \text{ cm}^2$ with an image resolution of 42 pixels/cm.

filter before being fit. The corresponding $\dot{m}''$ computed with Eq. 15 is given on the right hand side y-axis in Figure 3. As time progresses, the magnitude of $\dot{m}''$ is shown to decrease in Figure 3, as expected because the temperature of the water is continually cooling.

The results from 63 surfactant experiments and 103 clean surface experiments are now presented. The evaporation rate

per unit surface area $\dot{m}''$ is plotted against $\Delta\rho_{wv}$ in Figure 4 for each of the surface conditions explored. It is noted that in this figure (and in Figures 5 and 6), for the surfactant cases, individual data points are not presented, rather fits to the data are presented, as described in the previous section. Markers are superimposed at the beginning and end of these fits to distinguish the different cases. Figure 4 shows that at

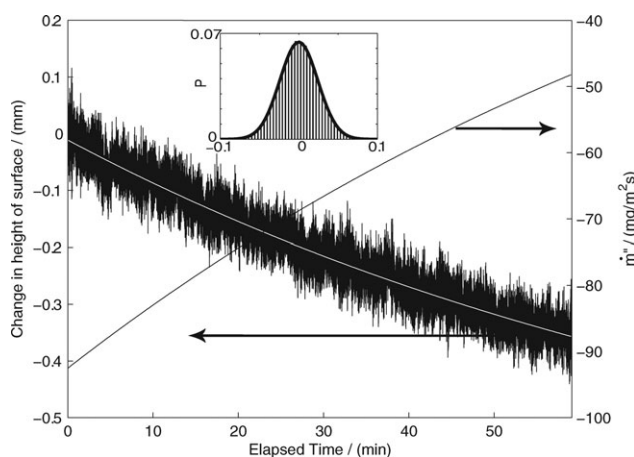


Figure 3. An example of the change in the height of the water surface (left ordinate) from a stearyl alcohol experiment on a $30.5 \times 30.5 \times 5 \text{ cm}^3$ tank.

The height of the surface is shown here for convenience which was computed from Y . The exponential fit of the form given by Eq. 16 is shown with the white line through the data, and is subsequently used to find $\dot{m}''$ (right ordinate) using Eq. 15. The PDF of the data fluctuation from the fit is shown in the inset with a zero mean, a standard deviation of 0.024 mm, and a skewness of 0.0272. A normal distribution is shown on the PDF with the solid line.

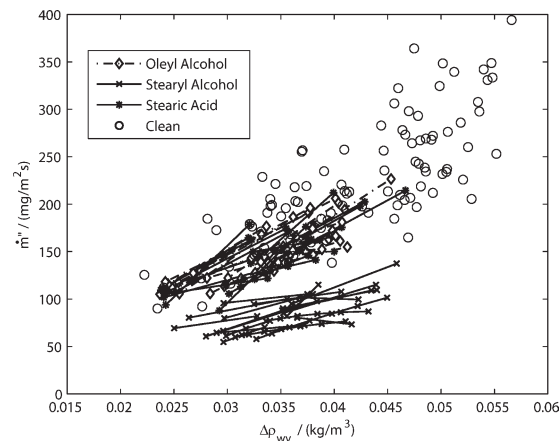


Figure 4. The evaporative flux of water for the various surface conditions as a function of $\Delta\rho_{wv}$

equivalent $\Delta\rho_{wv}$, less evaporation occurs (on the order of $\approx 50\%$) when a stearyl alcohol surfactant monolayer is present compared to any of the other surface cases. The large scatter of the clean surface data is attributed to the relatively short duration (5–10 min) of these clean surface runs, where the signal noise relative to the overall signal change is significant. The authors suspect that if the clean surface could be maintained for longer durations to allow for more data to be collected, then the scatter would be reduced.

Consideration was given to the possibility that air currents existed in the laboratory which could cause variability in m'' for all of the data (clean and surfactant conditions alike). However, measurements of air velocity were made around the tank and experimental facility with a TSI VelociCalc 9545 air velocity meter that was functional for $U > 0.20$ m/s, and no measurable air flows were detected.

The dimensionless groups Sh and Ra are obtained by processing the data presented in Figure 4 and these are plotted in Figure 5 over a three decade range of Ra. The Sh – Ra power law from the authors' earlier work^{18,24} is also pre-

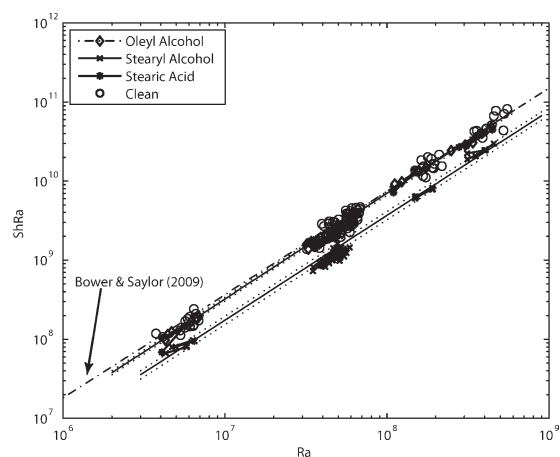


Figure 5. The dimensionless Sh – Ra results for the different surface conditions with results from earlier work.^{18,24}

The power law fits for the clean surface and the stearyl alcohol conditions are given by the solid lines, and the dashed lines indicate the 95% confidence intervals.

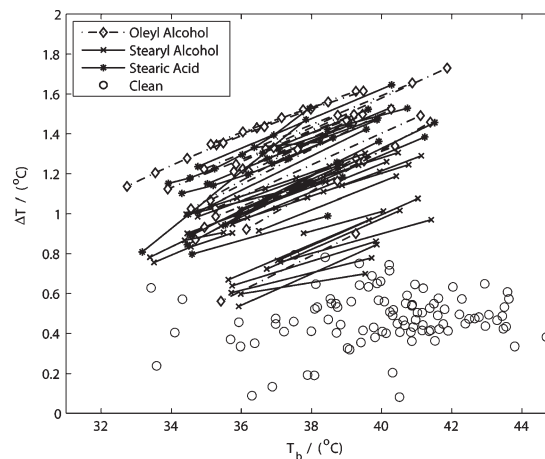


Figure 6. The water-side temperature difference ΔT and bulk temperature T_b .

For the clean surface runs, the average ΔT and average T_b are given. Figure courtesy of Bower and Saylor.⁵⁴

sented for comparison. Note that in Figure 5, the ordinate is $Sh \cdot Ra$ as opposed to Sh. Because T_∞ and ϕ are essentially constant, the independent variable for this investigation is essentially $\bar{T}_s$. It is desirable to have $\bar{T}_s$ affect only the parameter on the abscissa. However, $\bar{T}_s$ affects both Ra and Sh since it is related both $\Delta\rho/\bar{\rho}$ (found in Ra, Eq. 8) and $\Delta\rho_{wv}$ (found in Sh, Eq. 6). The product $Sh \cdot Ra$ minimizes the dependence of Sh on $\bar{T}_s$. This product gives

$$Sh \cdot Ra \propto \frac{\Delta\rho}{\Delta\rho_{wv}\bar{\rho}} \quad (19)$$

which changes by $\sim 10\%$ as $\bar{T}_s$ decreases during a typical experiment, compared to $\sim 60\%$ change in $\Delta\rho_{wv}$ (and thus a 60% change in Sh) if Sh and Ra are not multiplied. Whereas this treatment does not eliminate dependence on $\bar{T}_s$ from the ordinate, it does minimize it. The product $Sh \cdot Ra$ is still a measure of the efficiency of evaporative mass transfer since multiplying both sides of the original Sh – Ra power law (Eq. 10) by Ra gives

$$Sh \cdot Ra = BRa^{(m+1)} \quad (20)$$

Hence, m and B can still be obtained from a linear least squares fit to logarithms of both sides of Eq. 20

$$\log(Sh \cdot Ra) = \log(B) + (m+1) \log(Ra) \quad (21)$$

The resulting Sh – Ra power law fits are plotted in Figure 5 and summarized in Table 3. Actually, only the Sh – Ra fits for the clean surface and stearyl alcohol data are presented in Figure 5; the oleyl alcohol and stearic acid power law fits are excluded because they are indistinguishable from that of the clean surface.

Figure 5 shows that the stearyl alcohol surface condition yields lower Sh than any of the other cases at equivalent Ra. Hence, there is something about this surfactant that decreases the efficiency of evaporation for a given convection intensity (Ra). Figure 5 also shows that the oleyl alcohol, stearic acid, and clean surface cases yield essentially the same Sh – Ra behavior. This is surprising in that it suggests, at least in terms of evaporation efficiency, that these two surfactants give

Table 3. A summary of the Sh-Ra Power Law scalings B and m Determined from a Regression Analysis of the Experimental Data

Surface Condition	B	m	$CI_{95\%}$	S_{Sh}
	$Sh = B \cdot Ra^m \pm CI_{95\%}$			
Clean	0.144	0.336	5.9(%)	19(%)
Oleyl alcohol	0.146	0.334	6.9(%)	12(%)
Stearic acid	0.116	0.345	7.3(%)	13(%)
Stearyl alcohol	0.096	0.323	12.0(%)	21(%)

The 95% confidence intervals of the Sh-Ra fits and the standard deviations S of the data from the respective Sh-Ra fits are also provided in terms of percentages of Sh.

precisely the same behavior as a perfectly clean water surface. Finally, it is noted that the slopes of all the cases plotted in Figure 5 are very similar. This is evidenced in Table 3 by the fact that the exponents m are all very close to $1/3$. Hence, for all conditions, the rate at which Sh increases with Ra is independent of surface condition, at least for the conditions explored here. These points are further discussed in the next section.

Also presented in Table 3 are the 95% confidence intervals and the standard deviations S of the data from the Sh – Ra fits. The confidence intervals characterize the random error in the estimate of the true value of the Sh – Ra fit on account of scatter in the data and measurement uncertainty associated with $\dot{m}''$, $\bar{T}_s$, T_∞ , and ϕ .

Discussion

The main results from the Sh – Ra parameterizations presented here are: (1) at a given Ra, the stearyl alcohol case reduced evaporation from the clean case by approximately 50% and yields significantly lower Sh than all other cases over the range of Ra explored here, 2) the oleyl alcohol and stearic acid conditions yield essentially the same Sh – Ra results as the clean surface condition, and 3) the Sh – Ra power law exponent for all four surface conditions is close to $m = 1/3$.

Figure 5 shows a significant difference between the stearyl alcohol Sh and the other surface conditions revealing that stearyl alcohol decreases the efficiency of evaporation compared to the clean surface case (for a given Ra), and that oleyl alcohol and stearic acid monolayers do not. The effect of the surfactants on evaporation can be better defined by first creating a modified version of the prefactor B in Eq. 10: B^* . For each surface condition, B^* was obtained by forcing the Sh – Ra exponent to $\bar{m} = 0.334$ (the average exponent of all those shown in Table 3) and then refitting the data. The purpose of using $\bar{m} = 0.334$ is to force the slopes of the Sh – Ra fits to be equivalent forcing all of the difference between the different cases to be represented by the modified prefactor B^* . Next, we define a scaled mass transfer coefficient $\mathcal{H}$.

$$\mathcal{H} = \frac{B^* - B_o^*}{B_o^*} = \left(\frac{h_m - h_{m,o}}{h_{m,o}} \right)_{Ra, \bar{m}} \quad (22)$$

where $h_{m,o}$ is the clean surface condition mass transfer coefficient; B^* and $\mathcal{H}$ are listed in Table 4. Note that h_m and $h_{m,o}$ (B^* and B_o^*) in Eq. 22 are evaluated at equivalent Ra. Note that $\mathcal{H}$ is related to r_m via

$$\mathcal{H} = -h_m r_m \quad (23)$$

We choose to use $\mathcal{H}$ here, and not r_m , because $\mathcal{H}$ reveals the relative reduction in evaporative efficiency due to the

monolayer. The values of $\mathcal{H}$ presented in Table 4 show that stearyl alcohol is the only monolayer that significantly reduces h_m from that of the clean case. It causes a nearly 50% reduction in h_m while neither oleyl alcohol nor stearic acid significantly affect h_m at equivalent Ra relative to the clean case.

It should be noted that this reduction in h_m by stearyl alcohol is due solely to the barrier effect of the monolayer. This is because Eq. 22 is evaluated by comparing the mass transfer coefficients at equivalent Ra. When Ra are identical for two data points, this implies (for these experimental conditions), that $\Delta\rho$ (defined in Eq. 9) are identical which, in turn means that $\bar{T}_s$ is the same for both data points. This is because T_∞ was essentially constant during each experiment and varied by $S_{T_\infty} = 0.67^\circ\text{C}$ for all experiments conducted; for a given $\bar{T}_s$, change in T_∞ by the amount S_{T_∞} would cause h_m to vary by roughly 1%. This being the case, the only possible cause for the significant difference in h_m is the barrier effect, showing that, of the surfactant monolayers considered here, only stearyl alcohol provides a barrier effect. This result has not been obtained before.

In this work, the bulk and surface water temperatures are significantly larger than the air temperatures. This differs from the typical Langmuir trough configuration where the goal is to keep all temperatures as close to each other as possible.^{48,60,61} This air-side temperature difference results in natural convection flow in the air above the water surface. This should not be a concern in comparing different monolayers or surface conditions, however, so long as this comparison is done at equivalent Ra. If this is done, then the enhancement of evaporation due to these natural convection flows will be identical, and the only difference will be due to the surface condition.

The second main result of this work is that oleyl alcohol and stearic acid have essentially the same Sh – Ra power law as the clean surface condition. That is, for a given value of Ra, oleyl alcohol, stearic acid, and the clean surface conditions give the same Sh. At the outset of this investigation, the authors expected all three surfactant cases would yield Sh – Ra results that were measurably different from the clean case. The reason for this is that, the argument in the previous paragraph notwithstanding, the presence of each monolayer could restrict the flow of water at the very surface in different ways, which in turn could impact the flow of air above that water. Hence, it is possible, that even at constant Ra, a slight difference in Sh could exist between surfactants, even those without any barrier effect (e.g., stearic acid and oleyl alcohol). However, the current Sh – Ra mass transfer results prove otherwise, and, to the authors' knowledge, this is the first time that this has been clearly shown. An explanation for this can be obtained from the

Table 4. A summary of the mass transfer coefficient ratio $\mathcal{H}$ computed from Eq. 22 for the Different Surface Conditions

Surface Condition	$Sh = B^* \cdot Ra^{\bar{m}}$	
	B^*	$\mathcal{H}$
Clean	0.150	0
Oleyl alcohol	0.145	−0.03
Stearic acid	0.140	−0.06
Stearyl alcohol	0.078	−0.48

The mean coefficient B^* is determined for Sh-Ra by refitting the data with the exponent forced to the average $\bar{m} = 0.334$. The subscript L indicates that the length scale was defined as the ratio of the surface area to the perimeter.

characteristic velocities of air and water in the clean and surfactant cases. The characteristic velocity for water U at the surface was approximated by processing the IR imagery and tracking the movement of the sheet structures in the surface plane; for the clean surface $U \approx 0.5$ cm/s, for oleyl alcohol $U \approx 0.1$ cm/s, and for both stearic acid and stearyl alcohol $U \rightarrow 0$ cm/s. The characteristic velocity of air U_a is obtained by balancing the kinetic energy and the work done by buoyancy

$$\frac{1}{2} \rho U_a^2 = g \Delta \rho W \quad (24)$$

to give

$$U_a = \sqrt{2g \frac{\Delta \rho}{\rho} W} \quad (25)$$

For the experimental conditions explored here, $U_a \approx 10$ cm/s. As there is a no-slip boundary condition at the water surface, one could argue that a monolayer will affect the efficiency of evaporation by altering the flow of water at the surface, thereby affecting the air-to-surface velocity difference. However, the range of water surface velocities that exists in this experiment, $0 \text{ cm/s} < U < 0.5 \text{ cm/s}$, are all small compared to $U_a \approx 10$ cm/s. Thus, the effect of a surfactant on the air flow must be negligible, since the air velocity is much larger than the water surface velocity for all surface conditions, irrespective of whether a surfactant is present, or what type of surfactant is present. This explains why oleyl alcohol, stearic acid and clean surfaces all have the same Sh – Ra parameterization. Of course stearyl alcohol does give a unique Sh – Ra result, however this is the only surfactant which inhibits evaporation via a barrier effect as described earlier.

This barrier effect is due to the highly structured nature of the stearyl alcohol molecules at the interface. Lawrie and Barnes⁶¹ developed a surface pressure–temperature phase diagram for stearyl alcohol which shows that, for the experimental conditions herein, stearyl alcohol molecules are oriented normal to their surface and organize in hexagonal unit cells (i.e., the solid phase). Similarly, molecular dynamics studies due to Plazzer et al.⁶⁸ and Henry et al.⁵⁰ show that as the proximity of stearyl alcohol molecules increases, intermolecular forces cause the monolayer chains to change orientation and become well-ordered. This structured packing of surfactant molecules reduces the free volume at the interface through which water vapor can permeate. In this investigation, the barrier effect was not observed with either stearic acid or oleyl alcohol at π_{esp} . To the authors' knowledge, oleyl alcohol has never been reported to inhibit evaporation likely due to its liquid phase behavior; stearic acid can indeed inhibit evaporation as mentioned earlier but only when the monolayer is physically compressed above π_{esp} .^{11,16} Presently, it must be the case that the stearic acid monolayer lacks sufficient density at the surface to achieve a structured film that is capable of blocking water vapor.

Throughout this work, the authors have used W as the characteristic length when computing Sh and Ra via Eqs. 6 and 8. This scale was a natural choice since W was varied to obtain a wide range of Ra while maintaining a unity aspect ratio surface. To apply the current work to different surface geometries (including nonsymmetrical surfaces), the authors refer the reader to the Sh – Ra studies of Goldstein et al.²⁵ and Lloyd and Moran²⁶ who chose $L^* = A/P$ as a unifying

length scale. The Sh – Ra results presented herein are readily transferable to the results of Goldstein et al.²⁵ and Lloyd and Moran²⁶ since $W = 4L^*$ for the present case. Notably, B must be modified if L^* is to replace W as the length scale

$$B_{L^*} = B \left(\frac{64^m}{4} \right) \quad (26)$$

where B_{L^*} is the Sh – Ra coefficient corresponding to L^* . As discussed by Goldstein et al.²⁵ and Lloyd and Moran,²⁶ L^* can correlate mass transport from a variety of planforms and may be better suited than W for characterizing evaporation from non-square surfaces.

The Sh – Ra exponents obtained in this work were all very close to $m = 1/3$, showing that the rate at which Sh increases with Ra is the same for all surface conditions explored here. The average value of the four exponents from this study in Table 3 is $\bar{m} = 0.334$, essentially $m = 1/3$. It can be shown that when m is exactly $1/3$, the mass transfer coefficient is independent of the length scale W . That is, using Eq. 10 and setting $m = 1/3$, we get

$$h_m = \frac{\dot{m}''}{\Delta \rho_{\text{wv}}} = BD \left(\frac{g \Delta \rho}{\rho v \alpha} \right)^{1/3} \quad (27)$$

This result is also found in the study of natural convection heat transfer from a horizontal flat plate, which is a fairly exact heat transfer analogy to the mass transfer problem considered here. In this case, Sh is replaced by the Nusselt number, Nu, and the appropriate parameterization is a Nu – Ra correlation, also having an exponent of $1/3$ ⁶⁷

$$Nu \propto Ra^{(1/3)} \quad (28)$$

In fact, these two scenarios are different in that there is a zero velocity boundary condition at the surface of the solid plate for natural convection heat transfer from a heated flat plate, while in this study, the heated surface is a water surface that can have surface motion. The fact that the exponent is one-third for both cases suggests that the effect of the moving water surface is not significant in this study. This supports the analysis presented earlier, which shows that while the water surface can move, this motion is relatively small compared to the air motion. Hence, even if the water surface had absolutely no horizontal velocity component (as is the case for the heated flat plate), it is likely that the exponent m would still be one-third (or very close to it), explaining why this exponent is the same, regardless of whether the water surface is clean, or covered by a surfactant of any type.

Brief discussion is owed to the authors' earlier Sh – Ra results^{18,24} for evaporation from heated tanks of tap water where indigenous surfactant material was present at the surface (i.e. the surface condition was uncontrolled). Figure 5 shows this Sh – Ra power law result with the current findings. It can be seen that the magnitude of Sh from the earlier study is in good agreement with the present oleyl alcohol, stearic acid, and clean surface condition results. Where the results differ, however, is in the Sh – Ra power law exponent which was $m = 0.309$ in the prior work and $m = 0.334$ here. The earlier work used a mass balance and siphon apparatus. The rate at which water left the balance and flowed through the siphon tube into the water tank was measured, and a differential equation was used to correct for the resistance and inertance in the tube, thereby relating the measured

Table 5. Hypothetical Experiment Showing the Effects of the Surfactant Monolayers on $\dot{m}''$ Relative to the Clean Surface Condition

Surface Condition	T_b (°C)	ΔT (°C)	$\bar{T}_s$ (°C)	Ra	Sh	$\dot{m}''$ (mg/m ² s)
Clean	39	0.5	38.5	5.2×10^7	56	193
Oleyl alcohol	39	1.4	37.6	4.9×10^7	54	174
Stearic acid	39	1.4	37.6	4.9×10^7	52	168
Stearyl alcohol	39	0.8	38.2	5.0×10^7	29	99

For this demonstration, $T_b = 39^\circ\text{C}$, $T_\infty = 24^\circ\text{C}$, $\phi = 45\%$, and $W = 30.4$ cm.

rate to $\dot{m}''$. It is possible that fluidic resistance in the siphon tube caused more measurement error in $\dot{m}''$ as the magnitude of $\dot{m}''$ increased; for this reason, the rate at which Sh increases with Ra is less than for the present results. The laser-based method used herein provides a more direct and accurate measurement of $\dot{m}''$.

Up until this point, the present results have been discussed in terms of the dimensionless groups Sh and Ra. This permits an understanding of how the efficiency of evaporation changes (or does not change) when a surfactant is added, at a given Ra. For example, Figure 5 shows that stearyl alcohol is the only surfactant explored here which reduces Sh at a given Ra. One might misinterpret this to indicate that stearyl alcohol is the only surfactant explored which changes $\dot{m}''$, the evaporation rate. This is incorrect, at least for the conditions explored here where natural convection occurs within the water due to the fact that $\bar{T}_s < T_b$. In fact, for a given bulk water temperature T_b , all of the surfactants explored here reduce the evaporation rate, and it is this which is often of interest in actual applications. To get a better understanding of this, we first need to know how $\bar{T}_s$ changes when a surfactant is added to a clean surface. This is shown in Figure 6 which is a plot of the water-side temperature difference vs. T_b . Figure 6 shows that for a given T_b , ΔT is larger for the surfactant cases than for the clean case; in other words, $\bar{T}_s$ is lower when a surfactant is present. This is due to the ability of the surfactants to restrict surface motion, thereby allowing greater cooling of the surface.⁵⁴ To illustrate that all surfactants cause a reduction in $\dot{m}''$ when added to a clean surface (either by decreasing $\bar{T}_s$ or by directly inhibiting $\dot{m}''$), we consider a hypothetical case where the following natural convection conditions are prescribed: $T_b = 39^\circ\text{C}$, $T_\infty = 24^\circ\text{C}$, $\phi = 45\%$, and the horizontal dimension of the water body is $W = 30.4$ cm. These conditions are typical of the experiments performed in this investigation. For this analysis, the following procedure is used:

1. Using the prescribed T_b , the water-side temperature difference results in Figure 6 are used to approximate ΔT from which $\bar{T}_s$ is determined for all surface conditions.
2. With T_∞ and $\bar{T}_s$ known, Ra is computed from Eq. 8.
3. Ra is used to compute Sh from the experimentally determined Sh – Ra power law results in Table 3, for the surfactant being considered.
4. The net evaporative flux of water $\dot{m}''$ is computed from Sh using Eq. 6, and the data are compared with the clean surface condition.

The results from this procedure are presented in Table 5 which shows that all of the surfactants reduce $\dot{m}''$ compared to the clean case at equivalent T_b . This is true for oleyl alcohol and stearic acid even though these two cases share essentially the same Sh – Ra power law as the clean case. The surfactants are able to reduce the surface temperature slightly from the clean case due to the fact that water is immobilized longer at the surface. The oleyl alcohol, stearic

acid, and clean surface conditions share essentially the same Sh – Ra power law, however, have different evaporation rates which can be understood as follows: at equivalent T_b , all three of these conditions will result in different surface temperatures and hence different Ra and $\Delta\rho_{wv}$; having different values of Ra and $\Delta\rho_{wv}$, they necessarily will have different Sh and different evaporation rates. Stearyl alcohol also affects $\bar{T}_s$, but the large inhibition of $\dot{m}''$ in Table 5 is primarily caused by the physiochemical barrier effect of this monolayer which retards the passage of water vapor molecules across the interface.

The authors would like to emphasize that the above analysis will only apply when $\bar{T}_s < T_b$ such that natural convection occurs within the water bulk. We have demonstrated above that under this condition, all three surfactants reduced $\bar{T}_s$ (and consequently $\dot{m}''$) from the clean case at a given T_b by slowing the water layer near the surface. If it is the case that $T_b < \bar{T}_s$ such that the water is thermally stratified and convective transport is nonexistent, then oleyl alcohol and stearic acid will not affect $\bar{T}_s$ and only surfactants which impose the barrier effect (i.e., stearyl alcohol) will reduce $\dot{m}''$.

Conclusion

For the first time, the effects of surfactant monolayers on evaporation during convective transport have been studied using the dimensionless Sh – Ra power law parameterization. For all four surface conditions studied here, the dimensionless relationships were very close to $\text{Sh} \propto \text{Ra}^{1/3}$. The Sh – Ra power law results of the clean surface, oleyl alcohol, and stearic acid surface conditions were essentially the same within the confidence limits of the data. The stearyl alcohol case, however, yields Sh which are approximately 50% lower than Sh for the other conditions. Because Sh are compared at equivalent surface temperatures, it is shown that, of the three surfactants considered, only stearyl alcohol exhibits a barrier effect in its inhibition of evaporation. Finally, a demonstration was provided to illustrate that, despite sharing essentially the same Sh – Ra power law with the clean surface condition, adding either oleyl alcohol or stearic acid to a clean surface at a given T_b will decrease $\dot{m}''$ via a reduction in $\bar{T}_s$.

Acknowledgments

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