Influence of Hydrophilicity on the Thermal-Driven Surfactant Flow at the Air/Water Surface

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Supporting Information

**ABSTRACT:** A series of Triton surfactants with increasing number of ethylene oxide (EO) groups were applied to investigate thermal-driven surface flow. It was found that the thermal gradient is proportional to the number of EO groups on the surface. This correlation leads to the linear correlation between the surfactant structure and the driving force of the surface flow. The friction force, in contrast, follows a monotonic but nonlinear correlation with surfactant structure. The results demonstrate the possibilities to manipulate the surface flow, with potential applications in multiple-phase systems.

**INTRODUCTION**

The non-homogeneity of a surface, which can be easily created through a chemical/physical factor, can generate a surface flow.\(^1\) The surface phenomena include the well-known Marangoni’s and Bernard’s effects.\(^2\) Despite being weaker than the bulk flow, the surface flow can move floating objects such as an immiscible liquid drop.\(^3\) While the surface flow can be visualized at the macroscale, such as Bernard’s effects, the molecular nature remains unclear. However, it is generally agreed that the behavior of molecules near the air/water surface is different to that of solid/water during liquid flow.\(^4\) Recently, a novel experimental study has been able to demonstrate that the surfactant layer remains immobile in the presence of an electro-osmotic flow underneath the surface.\(^5\) We have found that thermal gradient on the air/water surface can generate a surfactant flow.\(^6\) A similar study has shown that a nanoparticle can be moved on the surface of a polymer solution via thermal gradient.\(^7\) Furthermore, it has been found that thermal gradient can deform the surfacetant structure.\(^8\) The surfactant flow can counter gravitational drainage and stabilize foam films in microfluidic devices.\(^10\) Collectively, these results indicated that there is a significant friction between the hydrophobic layer and the liquid underneath the surface. The friction should originate from the hydrophilic attraction between surfactant heads and the water molecules near the surface. While the surfactant flow on the surface can vary with concentrations,\(^11\) the molecular nature of the friction force and the role of the surfactant structure remain unclarified.

This study quantitatively explores the molecular origins of the phenomena by employing three Tritons with increasing hydrophilicity: Triton X-100, X-405, and X-705 with the number of ethylene oxide (EO) of 9.5, 35, and 55, respectively. The increasing number of EO will quantitatively increase the hydrophilicity and EO–water bonding of the surfactant layer. The controlled hydrophilicity of these surfactants has been utilized in many industrial applications.\(^12\)–\(^14\) The variation in hydrophilicity expectedly results in quantifiable changes in the friction coefficient and thus provides new insights into the molecular nature of the surface flow.

The study consists of two interconnected parts. First, the surface tension (ST) of the solution was experimentally measured at different temperatures. The results were then used to verify the relationship between the surfactant structure and the ST–temperature gradient. Second, the surfactant flow was experimentally monitored and modeled. The modeling parameters were then used to deduce the molecular impact on thermal and mechanical responses of the surfactant layer. Consequently, the surface flow of these surfactants can provide a quantitative description of the surfactant layer movement.

**THEORY**

**Impact of Temperature on ST.** From the literature, it is well-known that both ST\(^15\) and H-bonds\(^16\) are linearly varied with the temperature, from 0 to 40 °C (Figure 1). In the presence of surfactants, the water–water H-bond network near the surface is disrupted by surfactant molecules.\(^17\) In case of non-ionic Triton surfactants, the H-bond network at the surface is dominated by the water–EO H-bonds.\(^18\) As the temperature increases, it is expected that the bonding network is reduced linearly as with water–water H-bonds.
Mathematically, the impact of temperature on ST will be proportional to the number of EO

\[ \frac{d\gamma}{dT} = \varepsilon \Gamma \eta_{EO} \]  

where \( \varepsilon \) is energy per EO group (J/mol), \( \Gamma \) is the surfactant concentration at the interface (mol/m\(^2\)), and \( \eta_{EO} \) is the number of EO groups per surfactant molecules.

In this study, the slope of \( d\gamma/dT \) can be experimentally obtained for each surfactant. The data will be used to validate the thermal linearity as well as eq 1. Subsequently, the slope will be employed to model the ball movement.

**Driving Force of the Floating Object Movement.** The ball movement was studied using a previous setup (Figure 2a). In this setup, the heat source is from a thin tungsten wire, which allows a precise one-dimensional heat transfer (Figure 2b). Once a ST gradient is generated around the ball, the surface drives the ball toward the higher tension area. Similar phenomena have been reported with a floating liquid droplet. In these instances, the driving force is proportional to \( d\gamma/dy \), as presented in Figure 2. For a spherical solid ball, the driving force is given by

\[ F_a = -\frac{d\gamma(y)}{dy} \cos(\beta)A_s \]  

where \( \gamma(y) \) and \( A_s (\text{mm}^2) \) are the local ST at position \( y \) and the surface area of the contacting surface between ball and water, respectively. In the above equation, \( \beta \) is the contact angle between the air/water surface and horizontal axis. The angle is given by

\[ \beta = \theta - \phi \]  

where \( \theta \) is the contact angle between air/water surface and the solid material and \( \phi \) is the “immersion” angle. Because the ST gradient is very small (<1 mN/m), the contact angles, \( \beta \) and \( \theta \), are assumed the same between the left- and right-hand sides of the ball.

Because air/water ST is linearly dependent on temperature, the local ST is associated with the local temperature

\[ \gamma(y) = A_1 - A_2T(y) \]  

where \( A_1 \) and \( A_2 \) are surfactant-dependent constants.

The value of \( A_2 \) varies with the molecular nature and adsorbed concentration of the surfactants and can be determined by eq 1.

As the hotwire generates the uniform heat flux in all direction on the \( xy \)-plane, the temperature gradient is given by

\[ \frac{dT}{dr} = C_T \frac{1}{2\pi r} \]  

where \( C_T (\text{K}) \) is a constant accounting for the heat transfer in the air and \( r \) is the distance from the wire. The temperature gradient along the water surface is given by

\[ \frac{dT}{dy} = \frac{dT}{dr} \frac{dr}{dy} = \frac{C_T}{2\pi} \frac{2y}{y^2 + h_o^2} \]  

where \( h_o \) is the vertical distance from the wire to surface, which remains constant throughout the experiments.

Hence, eq 2 reduces to

\[ F_a = \frac{C_T A_1 A_2}{2\pi} \cos(\beta) \frac{y}{y^2 + h_o^2} \]  

While \( F_a \) is the driving force, the friction slowed down the movement of the ball. Previously, we have validated that a “dry” friction mechanism, in which the friction is independent on the velocity, is applicable to the ball motion. A constant deceleration, \( a_t (\text{m/s}^2) \), is acting against the motion. Consequently, the total acceleration of the ball is given as

\[ a(t) = \frac{E_{ff}y}{y^2 + h_o^2} - a_t \]  

where \( m_s \) is the mass of the ball and \( E_{ff} \) is the motion coefficient, which is defined as

\[ E_{ff} = \frac{1}{m_s} \frac{C_T A_1 A_2}{2\pi} \cos(\beta) \]

**Figure 1.** Influence of temperature on ST\(^{15}\) and H-bonds fraction\(^{16}\) of water.

**Figure 2.** (a) Ball motion experimental setup; (b) elemental force analysis of movement; and (c) schematic illustration of floating ball on surfactant solution\(^{20}\).
Hence, the motion is fully described by a system of two ordinary differential equations and can be solved numerically via the Euler method.6

It should be noted that $A_a$ (m$^2$) and $\beta$ are varied with surfactants and are determined experimentally. The value of $A_2$ (mN/m/K) is also determined independently from the slope of ST-versus-temperature profile. Consequently, the motion of the ball is experimentally monitored on different surfactant solutions. The motion is then modeled to get corresponding values of $E_{ff}$ and $a_f$. Hence, the influence of the surfactant structure on both driving and friction forces will be examined.

**RESULTS**

**Influence of the Surfactant on ST.** The ST of three systems was measured up to the critical micelle concentration (cmc) and is presented in Figure 3.

![Figure 3](image)

**Figure 3.** Equilibrium ST of three Triton surfactants up to the cmc.

The data were combined with the Gibbs equation to get $\Gamma_s$ (as showed in Table 1) using the common procedure.23 Previously, it has been showed that below the cmc, the surfactant flow is controlled by both adsorption and surface gradient.11 In this study, we used twice cmc to ensure the saturation of the surface layer. Hence, the ST at this concentration was used for temperature analysis.

As shown in Figure 4a, the ST of all solutions followed the linear reduction as expected. In the other words, $A_2$ is a positive constant for all surfactant solutions. In comparison to pure water, all three Triton solutions have a lower value of $A_2$. Furthermore, $A_2$ is linearly correlated with the product of $\Gamma_s n_{EO}$ (as shown in Figure 4b). The results validated the linearity of eq 1.

**Surface Temperature and Bulk Convection.** The thermal images (Figure 5) indicated a small gradient in temperature: the local temperature of the surfactant surface near the wire was just 8°C higher than room temperature. It has been reported that the convection near the surface is significant when contacting with a cool air.24 However, when a cool water contacting a warmer air, as in our setup, the thermal stratification was stable and no organized fluid motion was formed.12 The simulations showed that both horizontal and vertical velocities were insignificant, even at 15°C difference between hot air and cool water. On our system, the maximum difference was ~8°C and localized near the center. It should be noted that the bulk water in our system is more than 2 cm deep, comparing to 770 μm in the laser-induced thermal surface flow (Figure 6).7

To validate the influence of the bulk convection on the surface flow, the liquid motion was recorded for two scenarios: with wire over the water surface (as in Figure 1) and wire under the water surface. These two scenarios corresponded to the heating from the air phase and from the water phase, respectively. For these movies, iron(II) oxides particles, with an average diameter of ~8 μm, were suspended in the solution as tracers. In case 1, no organized motion was observed until the ball started moving. Between 2 and 4 s after the ball motion, an organized motion was observed, moving to the opposite direction (as demonstrated in Figure 5a). As the ball sped up, from 5 to 9 s, complicated convection was observed. In contrast, when heating under water (Figure 5b), an

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**Table 1. Adsorption, Thermal Response, and Shape Parameters of the Three Surfactants**

| surfactant | $n_{EO}$ | $\Gamma_s$ (mol/m$^2$) | $A_2$ (mN/m/K) | $A_a$ (mm$^2$) | $A_s$ (mm$^2$) | $\beta$ (deg) |
|------------|----------|------------------------|----------------|----------------|----------------|--------------|
| X-100      | 9.5      | $3.60 \times 10^{-6}$  | 0.240          | 0.217          | 1.733          | 65.6         |
| X-405      | 35       | $4.59 \times 10^{-6}$  | 0.274          | 0.259          | 1.674          | 60.6         |
| X-705      | 55       | $5.95 \times 10^{-6}$  | 0.302          | 0.448          | 1.297          | 35.1         |
organized and strong motion was clearly observed as soon as the power was turned on. The convection was in the same direction of the ball motion throughout the experiment. The recordings are in Supporting Information. The observations indicated that the surface motion was driven by the bulk convection in case of heating from below. When heating from the air phase, the ball motion generated a liquid flow in bulk depending on its velocity. This visual observation confirmed our model assumption that surface flow in Figure 1 configuration was not originated from the bulk convection.

**Influence of the Surfactant on Ball Floating Position.**

The equilibrium position of the ball is dependent on the ST and contact angle. For all systems in this study, the ball always floated. However, the position changed slightly with different surfactants (Figure 5). Qualitatively, the ball position is lower with the decreasing length of surfactant, which decreased the air/water ST (as evidenced in Figure 4a).

From the images, the contact radius $R_a$ (Figure 2c) was determined manually. Consequently, the contact angle ($\theta$) and the contacting area ($A_a$) were calculated for each of the conditions. Consequently, the value of $\beta$ was calculated from eq 3. The value of $\theta$ for Teflon is well-reported in the literature as 108°. Furthermore, the contacting area of the submerged part of the ball underwater, $A_a$ was also calculated and used for quantifying the friction coefficient in the following section. The shape parameters ($A_a$, $A_s$, and $\beta$) are included in Table 1 for the three surfactants, with the adsorption and thermal parameters. These parameters were fixed in the motion model.

**Influence of the Surfactant on Ball Movement.**

Figure 7 exhibits ball motion on different surfactant solutions. It is noteworthy that the motion was faster with a higher number of EO group. However, the ball stopped as the shortest distance at the highest EO groups (Triton X-705). The previous numerical model was applied, using Euler’s method with a step-size of 0.03 s, to obtain $E_g$ and $a_l$ (as tabulated on Table 2). The model fitted all three motions successfully. It can be seen that both driving and friction forces increased with increasing hydrophilicity. The values will be used to explore the molecular origin of the phenomena.

| surfactant | $E_g$ (mN/m/K) | $a_l$ (m/s²) |
|------------|----------------|--------------|
| X-100      | $9.81 \times 10^{-4}$ | $2.77 \times 10^{-3}$ |
| X-405      | $2.43 \times 10^{-7}$ | $6.98 \times 10^{-3}$ |
| X-705      | $1.03 \times 10^{-4}$ | $3.46 \times 10^{-4}$ |

**DISCUSSION**

To explore the molecular nature, the values of $E_g$ and $a_l$ were evaluated against the molecular structure of the surfactant layer. From eq 9, $E_g$ is a function of various constants. Amongst these constants, the contact area ($A_a$) and contact angle ($\beta$) varied with the surfactants, as tabulated in Table 1. The other parameters ($m_a$, $C_p$, and $d\epsilon/dT$) are independent of the surfactant. To highlight the role of surfactant hydrophilicity, the values of $E_g/A_a/\cos(\beta)$ were plotted against $\Gamma_n$ (Figure 8). It should be noted that the data in Figure 8 were obtained by all modeling steps (Figures 3, 4, and 7). However, the correlation was almost linear, which indicated that the number of EO groups is the driving factor of the motion (Figure 9).

On the other hand, the friction is determined by the contact area ($A_a$) and the friction coefficient between the ball and aqueous solution. It has been demonstrated that the adhesion force between Teflon and surfactant solutions are independent on composition and concentration of surfactants. Consequently, the friction coefficient is correlated with the viscosity of the surfactant layer and thus is also dominated.
driving force is proportional to the number of EO groups. In contrast, the friction coefficient was increased, monotonically but nonlinearly, with the number of EO groups on the surface layer. Both correlations are consistent with the thermal and rheological rule of EO bonding network. The results confirm the underpinning principles of thermal-surface flow and molecular origin of the friction between surfactant layer and liquid bulk. Furthermore, the new insights open a possibility to optimize the surface flow via changing the surfactant structure.

## EXPERIMENTAL SECTION

### Materials

Triton X-100, X-405, X-705 (70 w/w % in water), and sodium chloride were purchased from Sigma-Aldrich. A Teflon-coated tungsten wire, with an inner diameter of 0.2 mm, was provided by SDR Scientific, US. The Teflon ball with a diameter of 0.794 mm was purchased from the Hobby & Engineering Supplies, Australia.

### Surface Tension

The ST measurement consists of the two parts. First, the equilibrium ST was determined by applying the Wilhelmy plate method on a KSV Sigma 701 tensiometer (KSV Instruments Ltd., Finland) with an automatic micro-disperser. The adsorption density was then obtained by the Gibbs adsorption isotherm. Second, the ST was measured at different temperatures ranging from 20 to 40 °C by using the maximum bubble pressure method. Three Triton solutions with adding NaCl were utilized in this paper.

### Surface Flow

The previous setup was employed and is illustrated in Figure 2a. A series of Triton X solution with twice cmc and 3.5% NaCl were employed. A Teflon-coated tungsten wire was then placed above the surfactant layer to generate the thermal field. The position of the Teflon ball was tracked as a function of time by applying the edge detection function in MATLAB. All experimental data were analyzed subsequently to obtain the average fitting value and the standard deviation.

### Thermal Imaging

The temperature profile of the surface was captured via a Seek Compact Thermal camera (Seek Thermal, USA).

## CONCLUSIONS

The thermal-driven surface movement was investigated with three Tritons, with increasing number of EO groups. It was found that the thermal gradient of ST is proportional to the hydrophilicity, which is determined by the number of EO groups. The EO groups correspondingly governed the surface flow, by controlling both driving and friction forces. The

by the bonding of EO groups. In the literature, it has been verified that the viscosity of poly-ethylene oxide solution increased nonlinearly with the increasing number of EO groups. The higher number of bonds will increase the viscosity and friction coefficient. The viscosity-versus-molecular length should follow a power law as with common polymers. The data of $\alpha/\alpha_s$ are consistent with a power relationship between bond density and viscosity.

In summary, both driving force and friction are governed by EO bonds and thus are functions of $n_{EO}$ in the surfactant. The driving force is proportional to $d\tau/dT$, which is a linear function of the number of EO groups on the surface. The friction coefficient correlation with $n_{EO}$ follows a power-law. Qualitatively, Triton X-705, with the highest number of EO groups, increases both driving and friction forces. As the result, the ball moved faster but stopped at the shortest distance. The experimental and analysis also give a good estimation of the friction coefficient between the EO-based surfactant layer and underneath solution.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00733.

- Movement of the ball with the wire above the water surface (AVI)
- Movement of the ball with the wire underneath the water surface (AVI)

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### Notes

The authors declare no competing financial interest.

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