The Impact of Diffusion and Mixing in Expanding Fluid Drops on The Rate of Surface Tension Change

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Abstract

The dynamics of surface tension change in expanding drops of surfactant solution was studied using drop shape analysis. Experiments explored the dynamics of surface tension change resulting from the flow of surfactant-free water into a surfactant-containing drop. Experiments were conducted for two surfactants, one cationic (cetylpyridinium chloride) and one anionic (sodium octylbenzenesulfonate), both selected because they exhibit rapid adsorption/desorption, allowing for the study of mixing behind the expanding interface. Results were interpreted through the use of a spherical diffusion model designed to simulate drop expansion resulting from influx of surfactant-free water at the core of the drop. Best-fit diffusion constants were found to be consistent with reported molecular diffusion constants for the two surfactants, suggesting that hydraulic mixing within the drop does not play a significant role in the dynamics of surface tension change for the conditions studied. The results of the work have practical implications for applications where interface motion is induced by solute delivery, in that diffusion near the interface is likely to control the dynamics of interfacial tension reduction under many conditions.

1. Introduction

Rate limited adsorption at fluid interfaces has seen extensive study over the years. Many studies have centered around observed dynamic changes in surface or interfacial tension as surface active solutes (surfactants) adsorb at newly created interfaces. Experimental devices such as the bubble pressure tensiometer are capable of measuring interfacial tension in rapidly-formed interfaces, so can provide insight into the dynamics of how surface active solutes adsorb at interfaces [1-3]. Even static measurements of surface tension made using methods like drop shape analysis [4, 5] often observe a gradual approach to equilibrium surface tension that occurs over seconds to minutes or longer (e.g., [6, 7]). Rates of change of dynamic surface and interfacial tensions have been observed to vary significantly with different specific surfactants, as well as with different concentrations and other solution conditions [1-3].

A wide range of different models have been used to study dynamic surface tension changes, although most are based on recognition that the observed rate limited behavior is often consistent with the mathematics of diffusion. Ward and Tordai [8] proposed a model based on one-dimensional diffusion (in rectangular coordinates) to- and adsorption on a planar surface from a semi-infinite domain. Their interpretation of experimental data suggested that diffusion in the bulk was likely not the rate limiting process even in the case of very rapid equilibration. Subsequent analysis by Liu and Messow [9] using a more accurate solution to Ward and Tordai's equations came to similar conclusions, suggesting that bulk diffusion plays a significant role only at low concentrations.

One weakness with interpretations based on Ward and Tordai's model lies in its use of the one-dimensional diffusion equation in rectangular coordinates, an approach now recognized to yield erroneous interpretations in drops. Models published since Ward and Tordai's work

have taken other diffusion-based approaches. For example, Filippov and Filippova [10] developed equations for adsorption at the interfaces of spherical drops, based on diffusion limited motion in both the bulk and in the adsorption isotherm. Yang and Gu [7] developed a Galerkin finite element solution to solve diffusion and adsorption in a static drop shape defined by a pendant drop profile. In their work they analyzed both the Ward and Tordai [8] and spherical Filippov and Filippova [10] diffusion solutions, concluding that the Ward and Tordai equation worked poorly in a pendant drop, while the predictions of the spherical Filippov and Filippova solution were significantly closer to those determined based on the more accurate geometry used in the finite element solution. Yang and Gu [7] observed dependence on both drop size and syringe needle size in their simulations of adsorption rate, both the result of the impact on the distance over which bulk surfactant diffuses as it is depleted by interfacial adsorption.

While substantial efforts have been made in the study of the dynamic processes that underlie dynamic interfacial tensions, little is known about the mixing and diffusion that occurs behind an advancing interface. This is important because many practical applications of surface and interfacial tension modification (for example, subsurface remediation of separate phase organic liquids, oil recovery) depend on using a surface active solute to change the interfacial tension of a moving interface.

The focus of the work described here was on examining mixing and diffusion within expanding pendant drops, to understand the impact on the dynamics of the resulting surface tension change. Specifically, drops were formed containing surfactant solution, and then expanded with surfactant-free water to study the influence of mixing and diffusion on the dynamics of the interfacial tension decrease at the surface resulting from dilution within the

drop. Two ionic surfactants were used, one anionic and one cationic. A spherical advection-diffusion model with expanding boundaries was developed to simulate solute behavior in the expanding drops, and used to interpret the results of experiments.

2. Materials and Methods

2.1. Surfactants

The two surfactants selected for the work were cetylpyridinium chloride (CPC), a cationic surfactant, and sodium octylbenzenesulfonate (SOBS), an anionic surfactant. Both were selected because their adsorption equilibrates at interfaces rapidly, allowing experiments to focus on understanding mixing and diffusion within expanding drops (see the accompanying *Supplementary Material* section). Both CPC and SOBS were purchased from Sigma-Aldrich (St. Louis, MO). Both surfactants had stated purities of 99% or higher as received, but were further purified by foam fractionation to remove any highly surface active impurities [11]. Experiments with CPC were conducted without added salt, while experiments with SOBS were conducted in the presence of 0.1 M sodium chloride (NaCl) to increase the efficiency of the highly-hydrophilic SOBS for interfacial tension reduction. All drop expansion experiments were conducted below the CMCs of the two surfactants (9.6×10^{-4} M for CPC in water, 2.4×10^{-3} M for SOBS in 0.1 M NaCl).

2.2. Surface Tension Measurement in Static and Expanding Drops

All surface tensions were measured using the custom drop shape analysis system and software described in earlier work [12]. Equilibrium measurements of CPC surface tensions were conducted by creating pendant drops with a Cole-Parmer Gilmont (Vernon Hills, IL) 2 mL

micrometer syringe with a 13 gauge square-end needle, and then imaging the drops over time at approximately 20 sec. intervals after an initial brief pause to allow vibrations to dissipate. Three images were collected over the course of approximately one minute, and were analyzed by automated fitting of the Bashforth-Adams equation [12]. Equilibrium data for SOBS in the presence of 0.1 M added NaCl were taken from previous measurements conducted in our laboratories [13]. No systematic variation in measured surface tension was observed over time for either system in the time scale of the measurements taken.

Experiments examining drop expansion were conducted in an enclosed aluminum optical cell with glass windows. The internal dimensions of the cell were 2.5 cm high $\times$ 3 cm wide $\times$ 1.5 cm deep. The cell was enclosed during the experiment to minimize drop evaporation. Additional water was placed inside the cell to further reduce evaporation. A short section of 13-gauge hypodermic tubing passed through the top of the cell and was connected externally to a syringe pump by way of 1/16" outer diameter PEEK HPLC tubing. Experiments were conducted as follows: surfactant free water (or 0.1 M NaCl in the case of SOBS experiments) was pumped from the syringe pump to create a small initial drop, typically 0.3-0.5 μ L, as determined by drop shape analysis (Figure 1 A). A 10 μ L syringe with fine gauge needle was then used to add approximately 5-7 μ L of surfactant solution to the drop, expanding its size (Figure 1 B). The syringe pump was immediately started, and pure water (or 0.1 M NaCl in the case of SOBS experiments) was pumped into the drop, causing it to expand (Figures 1 C-F). For the work described here, drops were expanded at a rate of approximately 3.9 μ L/min, as determined from image analysis of expanding drops. Images were captured at 4 second intervals over the course of the experiment. Drops were allowed to expand until they became too large and detached from the hypodermic tubing. It should be noted that experiments like those described here could also

be conducted using a coaxial capillary pendant drop device (e.g., [14-16]) rather than the manual injection method described above (Figure 1B), although the authors are not aware of published reports of its use for that purpose.

Evaluations of simulations against equilibrium data were based on comparison with fits to equilibrium surface tension data based on the Szyszkowski Equation (a combination of the Langmuir and Gibbs adsorption equations, Eq. 1) [17].

$$\Delta\gamma = mRT\Gamma_{max}\ln(1 + KC) \quad (1)$$

where $\Delta\gamma$ is the difference between the surface tension of pure water and the surfactant solution, Γ_{max} is the maximum surface excess of adsorbed surfactant, K is a Langmuir adsorption constant, and C is the surfactant monomer concentration. The multiplier m is either 1 or 2 depending on the type of surfactant and amount of added salt (1 for an ionic surfactant with excess salt or for a nonionic surfactant, 2 for an ionic surfactant with no added salt). Fit Szyszkowski equation values for the two surfactants under the conditions studied were: CPC ($m=2$, $\Gamma_{max}=3.09\times 10^{-6}$ mol/m², $K=5398$ L/mol), SOBS with 0.1 M NaCl ($m=1$, $\Gamma_{max}=4.39\times 10^{-6}$ mol/m², $K=7178$ L/mol).

2.3. Drop Expansion Model

Drop expansion was simulated using a diffusion model based on the diffusion equation in spherical coordinates (Eq. 2):

$$\frac{\partial C}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) \quad (2)$$

where C is concentration of solute, t is time, and r is distance from the center in a spherical domain. Eq. 1 was solved using a fully implicit shell-centered finite volume formulation [18]. Neumann boundary conditions were used in the solution at both $r = 0$ (the center of the drop) and

$r = R$ (the outside edge of the drop) to simulate the case of no diffusive flux across the two boundaries. The drop was discretized as concentric shells of equal volume (and thus, with decreasing Δr with expanding radius). Advection caused by water entering the center of the drop was simulated by adding additional shells to the outside of the drop at intervals dictated by the flow rate, shifting simulated concentrations outward by one shell, and writing a zero concentration value into the innermost shell – essentially simulating a constant flux of zero concentration water to the center of the drop. Because the shells all have the same volume, mass is conserved when shifting concentrations between shells. Calculated masses were unchanged over the course of simulations to more than 12 significant figures. For all simulations conducted for this work, a shell size of approximately 0.1 μL was used, but that size was automatically adjusted slightly for each experiment so that an integral number of shells could exactly represent the starting volume of each drop.

Simulations were conducted in Python 2.7 using solvers from the NumPy scientific programming library.

3. Results and Discussion

Figure 2 shows the measured surface tension for an expanding CPC drop as a function of the average surfactant concentration in the drop (the total mass of surfactant in the drop divided by its volume). The data in Figure 2 correspond to the same CPC system for which images are shown in Figure 1, i.e., a starting concentration of 3.1×10^{-4} M, initially diluted by adding 6.1 μL of 3.4×10^{-4} M solution to a 0.36 μL drop of water (Figures 1A, B). Letters C, D, E and F in Figure 2 correspond to the image subfigures in Figure 1. Note that when surfactant is added to the drop (C) there is an initial rapid decrease in surface tension, resulting from the mixing that occurs as a

result of the rapid initial drop expansion and corresponding adsorption of the added surfactant. After approximately 30 seconds (the rightmost 7 red circles) the measured surface tension reaches a minimum near 56 mN/m where it remains for an additional approximately 30 seconds as the drop continues to expand, and then (point D) surface tension begins increasing monotonically with further expansion as the concentration in the drop is further diluted by incoming pure water. Of perhaps greatest interest in Figure 2 is the fact that the observed relationship between surface tension and average concentration do not follow the equilibrium surface tension data, despite the fact that the drop was expanded very slowly (the elapsed time between points C and F (Figs. 1, 2) was 6.4 minutes for a volume change of 24.7 μ L).

Figure 3 shows average concentrations over time for CPC drops with five different starting concentrations. The trends in Figure 3 are parallel to those in Figure 2, and in all cases, the observed curves do not follow the equilibrium surface tension curves.

The results in Figures 2 and 3 strongly suggest that despite the slow flow rate and small distances between the drop core and surface, the contents of the drops are not completely mixed. Note that CPC itself adsorbs rapidly at interfaces; surface tension of a new drop formed with a CPC solution equilibrates within the time it takes for the drop to stabilize (seconds). Furthermore, gradually expanding a CPC drop without changing its concentration (i.e., expanding it by pumping additional solution rather than pure water) produces no observable change in surface tension. As such, the results in the figure are consistent with a case where the concentration at the core of the drop is lower than the concentration at the drop surface, and, as a result, the surface tension is lower than would be predicted based on average surfactant concentration alone.

To better quantify and understand this phenomenon, simulations were conducted based on the spherical diffusion model described in Sec. 2.3. The simulations started with an initial CPC concentration in the drop calculated from the initial dilution of added surfactant (i.e., Fig. 1 A, B). For purposes of this work adsorption at the interface was assumed to be instantaneous, in complete equilibrium with surfactant in the outer shell in the model. Application of the model involved matching measured interfacial tensions over time with the simulated surfactant concentration at the surface at the same times and volumes for a given diffusion constant, D .

Figure 4 illustrates the model for a starting CPC concentration of 3.1×10^{-4} M – the same concentration used in Figs. 1 and 2. For large D values (e.g., 10^{-8} m²/s in the figure) the surfactant in the drop approaches completely-mixed, and the curves are close to the average concentration curve. (Note that D values of 10^{-7} m²/s or larger (not shown) produce surface concentrations essentially equivalent to complete mixing.) For smaller D values, the extent of mixing in the drop during expansion decreases, shifting the curves in Figure 4 to the right. That is, small D values cause concentrations at the surface to change more slowly, remaining high as the drop expands. If D is sufficiently small (e.g., 10^{-11} m²/sec in the figure), sufficiently little mixing occurs that the surface concentration in the drop remains essentially constant, yielding a vertical curve. In between these extremes, there is a value of D – in this case 3.37×10^{-10} m²/s – that corresponds to a curve that closely matches the equilibrium curve. The match between the simulated and equilibrium curves is an indication that the corresponding D accurately describes the extent of mixing that occurs within the drop.

Figure 5 shows simulation results for the five CPC concentrations in Figure 3 at a single D of 3.37×10^{-10} m²/s. This value of D was determined to provide the least-squares best fit between the simulated surface concentrations and concentrations calculated from the

Szyszkowski equation for the experimentally measured surface tensions. (Note that error was minimized in the log concentration scale.) Note that the magnitude of D determined through this fit is very similar to, and slightly smaller than, the molecular diffusion constants of $6.3 \times 10^{-10} \text{ m}^2/\text{s}$ and $8.4 \times 10^{-10} \text{ m}^2/\text{s}$ reported by Verma et al. [19] and Leaist [20], respectively, for CPC monomers, although slightly larger than the $1.21 \times 10^{-10} \text{ m}^2/\text{s}$ suggested by the calculations of Atkin et al. [21]. The similarity is a strong indication that the primary mode of mixing within the expanding drop is molecular diffusion rather than hydraulic mixing induced by the flow of water into the drop. If an appreciably higher value of D were required to simulate the data (e.g., an unrealistically large value for a molecular diffusion constant, such as 10^{-8} or $10^{-9} \text{ m}^2/\text{s}$) it would be a strong indication that additional mixing was occurring within the drop.

It is important to emphasize that this result (i.e., mixing controlled by molecular diffusion) might not be expected to hold under conditions of extremely rapid interface expansion, where internal hydraulic mixing would almost certainly contribute to more rapid equilibration than would be predicted from diffusion alone. Additional factors, such the syringe diameter and resulting inflow velocity could also potentially impact the nature of mixing in the drop. In the context of this work, the inlet water had a velocity of approximately 1.5 mm/min, and the radial expansion velocity of the outer drop surfaces ranged from approximately 0.1 to 0.2 mm/min, depending on the size of the drop. (Note that the coaxial dye mixing experiments reported by Ferri et al. [16] involved an exchange flow rate greater than 26 $\mu\text{L}/\text{min}$, approximately 7 times the volumetric flow rate used in the drop expansion experiments in this study.)

While faster flow could potentially be expected to induce a transition from diffusion-dominated mixing to hydrodynamic mixing, it is interesting to consider the implications of the result for even slower expansion than was studied here. It is reasonable to expect that there is a

rate below which an expanding drop can be considered completely mixed, i.e., the concentration can be considered uniform throughout. However, simulations indicate that that rate is *exceedingly* small. For example, for expansion of a CPC solution, simulations indicate that a 1000× smaller volumetric flow rate (e.g., to 0.0039 $\mu\text{L}/\text{min}$) would be needed to create conditions where the average concentration in the drop remained within 1% of the concentration adjacent to the surface. The small magnitude of that flow rate means that for all practical purposes, formation of interfaces caused by slow expansion will result in concentration gradients.

Figure 6 shows the spatial distribution of CPC concentrations within the drop, predicted by simulation with $D = 3.37 \times 10^{-10} \text{ m}^2/\text{s}$. The four plots shown correspond to the four drop images in Figures 1 C, D, E and F. It is apparent from the Figure that even for the very slow expansion rate used (approximately 3.9 $\mu\text{L}/\text{min}$), much of the surfactant mass remains near the outer surface of the drop during the process of expansion, and the inner core of the drop is essentially pure water.

Figure 7 shows expansion data for five different starting concentrations of SOBS in the presence of 0.1 M NaCl. As was observed with the drops containing CPC (Figure 3), the curves of average concentration vs. interfacial tension in Figure 7 remain below the equilibrium curve over the course of drop expansion, an indication that complete mixing is not occurring within the drop.

Figure 8 shows best fit simulation data for the SOBS system. In the case of SOBS, a value of $D = 4.50 \times 10^{-10} \text{ m}^2/\text{s}$ provides the best fit to the equilibrium data. This value agrees favorably with the value of $6 \times 10^{-10} \text{ m}^2/\text{s}$ reported by Lindman et al. [22] for SOBS monomer

diffusion, suggesting that, as was the case with CPC, molecular diffusion is likely the primary mixing mechanism in the expanding SOBS drops.

4. Conclusions

The results of this work suggest that molecular diffusion controls mixing within slowly-expanding aqueous drops; hydrodynamic mixing caused by inflow of water does not appear to be a significant factor in the dynamics of drop surface tension equilibration. Despite the small distances involved and slow expansion rates, an assumption of complete mixing within the drop provides a very poor prediction of surface tension dynamics.

The significance of this result is that for any application where interface motion results from flow, interfacial behaviors may not be well predicted by fluid properties small distances – even mm – from the interface, but rather may be limited by bulk diffusion. While conditions of rapid expansion may involve some hydrodynamic mixing which would be more rapid than diffusion-limited mixing, a range of flow rates covering several orders of magnitude exists for which complete mixing behind an interface cannot be practically assumed. This phenomenon may be important in any application that depends on interaction of a solute with a moving fluid interface. It is worth noting that this effect could potentially be exacerbated in systems with higher concentration micellar surfactant solutions, because the diffusion coefficients for micelles can be an order of magnitude or more lower than those of monomers. However, this effect could to some extent be mitigated by the use of concentrations orders of magnitude above the CMC, increasing the driving force for diffusion.

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Figure Captions

Figure 1. Selected images from drop formation and expansion for aqueous CPC. Added CPC concentration 3.3×10^{-4} M. Water flow rate = $3.87 \mu\text{L}/\text{min}$.

Figure 2. Measured surface tension (γ) vs. average concentration in an expanding drop for the CPC system shown in Figure 1. Letters correspond to subfigures of the corresponding images in Figure 1. Equilibrium data and Szyszkowski equation fit to equilibrium data are also shown for comparison.

Figure 3. Measured surface tension (γ) vs. average concentration in expanding drops for five different starting CPC concentrations. Equilibrium data and Szyszkowski equation fit to equilibrium data are also shown for comparison.

Figure 4. Measured surface tension (γ) vs. calculated surface concentration in an expanding drop for the CPC system shown in Figures 1 and 2. Calculated surface concentrations are shown for different D values.

Figure 5. Measured surface tension (γ) vs. calculated surface concentration in expanding drops for five different starting CPC concentrations. Calculated surface concentrations correspond to $D = 3.37 \times 10^{-10} \text{ m}^2/\text{sec}$, the least-squares best-fit value for the data.

Figure 6. Calculated spatial configuration of CPC for the system in Figures 1 and 2, based on $D = 3.37 \times 10^{-10} \text{ m}^2/\text{sec}$. Darker shading corresponds to higher concentration. (Black = 3.1×10^{-4} M, White = 0 M). Letters correspond to drop images in Figure 1 and data points in Figure 2.

Figure 7. Measured surface tension (γ) vs. average concentration in expanding drops for five different starting SOBS concentrations. Equilibrium data and Szyszkowski equation fit to equilibrium data are also shown for comparison. *Equilibrium data from Chen and Kibbey, 2006.

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Graphical Abstract

Surface tension was measured in drops of surfactant solution expanded by injection of surfactant-free water. Analysis with simulations suggests that molecular diffusion controls the dynamics of surface tension change for these systems.