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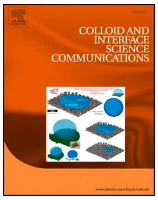

Rapid Communication

Proximity-induced surfactant aggregation

Zechen Zhang, Jared R. Arkfeld, William A. Ducker *

Department of Chemical Engineering and Center for Soft Matter and Biological Physics, Virginia Tech, Blacksburg, VA 24061, USA

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ABSTRACT

We describe surfactant aggregation (micellization) that is induced by the proximity between two interfaces. Under conditions where surface aggregation does not occur for a single interface, we observe surfactant aggregation between two glass solids that are separated by a thin aqueous film that is <30 nm thick. The surfactant is dodecyltrimethylammonium bromide (DTAB). Interfacial aggregation occurs at 1/100th of the critical micelle concentration (cmc) and is likely an electrostatic effect of the introduction of a second interface. Nile red, a solvatochromic dye, is used to indicate aggregation.

The stability of colloids frequently depends on the existence of an electrostatic double-layer force [1,2]. Since the 1970's colloid science has known that the electrical potential of an interface is altered by the presence of a second interface. A seminal paper by Ninham and Parsegian [3] described the concept of "charge regulation" of surfaces during the decrease in separation between two interfaces, which leads to distance-dependent surface charge and potential, rather than a fixed charge or potential. Since that time, models of charge-regulated surfaces have been extensively employed for calculation of double-layer forces that are used to understand colloidal stability (e.g., [4,5]). In particular, Chan et al. [5], described a facile method for calculating the charge-regulated interaction, and described two limits of the double-layer interaction: an upper energy limit of constant charge and a lower limit of constant potential. These limits applied under the assumptions of their model, which was that the chemical potential of the adsorbing species depended only on a standard state plus electrostatic interactions; there was no other density-dependent term.

On the other hand, it is well known that many species have non-electrostatic interactions. For example, surfactants associate to form micelles because of the hydrophobic effect. For this reason, surfactant isotherms have features that are distinct from adsorption isotherms of simple ions. In particular, there is frequently a sharp rise in adsorption as a function of bulk concentration that is attributed to surfactant aggregation [6,7]. This effect has been modelled by the Frumkin adsorption isotherm [8], which includes a surface density-dependent term to model hydrophobic interactions. The effect of hydrophobic interactions can be sufficiently strong that they lead to charge-reversal of solid-liquid interfaces [6,9], e.g., an anionic surface can be made cationic by adsorption of a cationic surfactant.

Despite the widespread knowledge that charge reversal can occur and the necessity of a non-electrostatic density dependent term to quantitatively describe adsorption of surfactants to solid-liquid interfaces, it has been common practice to model double-layer forces between two solid-liquid interfaces in surfactant solution without a non-electrostatic density-dependent term in the chemical potential [10–14]. Neglecting this term leads to the idea of constant potential being the lower limit of charge regulation and therefore the least repulsive electrostatic force. Combined with the idea that surface forces are additive, this can lead to the conclusion that measured forces that are less repulsive than the constant potential case are indicative of additional forces such as hydrophobic forces (e.g. [10,12],). It is, therefore, extremely important to determine whether charge regulation of surfactants can lead the potential to fall below the constant potential case and whether aggregation can occur due to confinement.

In this letter, we provide direct evidence that surfactant association can be driven simply by bringing two interfaces together. It is a form of confinement-induced change [15,16] that we call proximity-induced aggregation. We do not directly show that the surface potential decreases, but we do directly show that aggregation occurs, and therefore, that density-dependent interactions occur. This is the required behavior for interactions where the electrical potential decreases. We show that the surface structure that is present on confinement is completely different than the structure of isolated surfaces, and therefore it is perilous to assume that the structure remains invariant as two interfaces approach. This change in structure is not minor but can be a change from non-aggregation to aggregation state. Prior research shows that the

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* Corresponding author.
E-mail address: wducker@vt.edu (W.A. Ducker).

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geometry of surfactant aggregates above the cmc can be altered by confinement, e.g., [17] but not that a switch from not-aggregated to aggregated on confinement.

The overall concept of proximity-induced aggregation is shown schematically in Fig. 1. Charge regulation driven by electrostatics alone can lead to an increase in adsorption, but when the short-range hydrophobic effect is present (e.g., for surfactants), aggregation may occur. The extra charged surfactant that adsorbs during aggregation leads to a decrease in magnitude of the surface potential. Another way of putting this is that the association of charged surfactant is hindered by the repulsion between headgroups. In this case, the presence of an additional negative electrical field from negative ions on a second interface decreases the energy cost of aggregation of cationic surfactant and allows surfactant aggregation at a lower concentration.

Prior work provided *indirect* evidence of proximity-induced aggregation through surface forces measurement [18–22] and modelling [23]. For cationic surfactants on (anionic) silica or glass, for example, force measurements are consistent with adsorption of surfactant as two silica-aqueous interfaces move closer together [18–21]. The increase in adsorption density due to charge regulation may make the surfactant surface density sufficiently high to initiate surface micellization and cause a disproportionate change in the surface potential. In this way, an electrostatic force with characteristic length of the Debye length may trigger a hydrophobic effect which then affects the double-layer force. That is, the (long ranged) double-layer and (short ranged) hydrophobic effect are coupled. Such effects have been shown in Self-Consistent Field Theory (SCFT) calculations [23] and modelled using the constant regulation approximation [24].

Here we provide direct evidence of proximity-induced surfactant aggregation using fluorescent emission microscopy of a solvatochromic dye, Nile Red [25]. The emission from Nile red is much greater in a hydrophobic environment than in a hydrophilic environment. We use 3.14 μM (1 mg/L) Nile red to test for the presence of aggregation of the cationic surfactant, dodecyltrimethylammonium bromide (DTAB), as a function of the separation between two (anionic) glass wafers. All solutions used in the experiments contained 0.1% *v*/v ethanol for solubilization of Nile red in water. DTAB (Sigma Aldrich, 98%) was recrystallized three times from acetonitrile (Spectrum Chemicals, 99.9%). The surface tension of the purified surfactant did not exhibit a minimum in a plot of surface tension as a function of concentration.

Instead of changing the separation with time, we measure a single system at equilibrium that has a variety of separations between the glass wafers. We create this system by simply bonding two glass wafers face to face (See Supplementary Material, S1 Details of the Experimental Method) [26]. Because of imperfect bonding at the edge, there is a gently sloping (slope ∼ 1/1000) crack. When viewed from the edge, the crack is approximately triangular (See inset in Fig. 2B). When the wafer is viewed through the flat side, each pixel in the image approximately represents two parallel flat surfaces. An image contains a set of pixels, where the separation between the wafers is almost invariant in one direction (*y*) and changes by about 1 nm per pixel in the other direction (*x*). At equilibrium, with nothing moving, we simultaneously measure the fluorescence (i.e., the hydrophobic state) in the thin film at all *x*-*y* positions and therefore at all separations. Two microscopy methods were used: interferometric microscopy to determine the film thickness, and fluorescence microscopy to detect the surfactant aggregation. Taken together, the aggregation state is known as a function of film thickness. Details of the technique are described in our previous work [26] and in Supplementary Material S1.3. Surfactant aggregation at interfaces can depend on impurities, so we first recrystallized the DTAB (≥98%, Sigma-Aldrich) three times to remove impurities. The recrystallized DTAB has a critical micelle concentration of 14 mM (Supplementary Material S2. Measurement of Critical Micelle Concentration of DTAB).

As a prelude to measurements in a crack, we measured the variation of fluorescence emission of Nile red *in bulk aqueous solutions* as a function of DTAB concentration using a HORIBA FluoroMax®-4 spectrofluorometer. Below the DTAB critical micelle concentration (cmc), the emission of Nile red was negligible and above the cmc the emission was high (see Fig. 2A), thus demonstrating the ability of Nile red to detect micelle formation within DTAB solution.

From this point, all results are for aqueous solutions confined in a thin (0–400 nm) film between two glass–aqueous interfaces at about pH 6.7. We first tested the behavior of Nile red in the crack when the DTAB concentration was 6 mM, which is approximately half of the cmc. Note that our experiment gives the total emission from both the interface and the “bulk liquid” in the 0–400 nm of aqueous solution between the crack. If we were to measure fluorescence of a thin film above the cmc, we would see emission from micelles in the “bulk” solution. By measuring below the cmc, we do not have this interfering effect. Owing to the negative surface charge on glass in water, we expect surface aggregation below the cmc. By measuring at 6 mM, we measure only surface aggregation and not bulk aggregation.

Our results show no emission at zero thickness (there is no space for the DTAB and Nile red) and almost uniformly high emission at finite thicknesses indicating surface aggregation (Fig. 2B). This experiment is our positive control; it demonstrates the ability to observe surface aggregation of surfactant by the use of Nile Red. The slight increase of intensity as a function of separation is an interference effect (see [26]) and is not evidence for increasing hydrophobicity as a function of film thickness.

Knowing that Nile red reveals the aggregation state of DTAB, we investigated lower concentrations of DTAB, where there was no emission when the surfaces were far apart, i.e., below the critical surface aggregation concentration of an isolated solid–water interface. Our results focus on 0.10 mM DTAB, which is 0.7% of the cmc. The experiment was done in two parts: (1) a control solution containing only 3.14 μM Nile red and then (2) a solution containing DTAB and Nile red was introduced into the flow cell and allowed to equilibrate in the crack.

The control experiment with no surfactant (Fig. 3A) shows no fluorescence at small film thicknesses. Unfortunately, there are a number of bright patches in thicker parts of the film. These are likely to be hydrophobic contaminants that deposited onto the glass surface during the

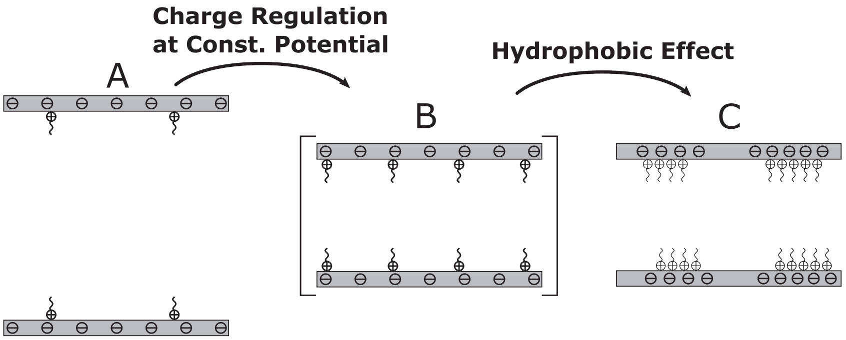

Fig. 1. Schematic of proximity induced adsorption for cationic surfactants on an anionic solid. A. At large separation, the surfactant is below the critical surface aggregation concentration and only monomers are present. B. At smaller separations, according to regulation of simple ions at constant potential, there will be a greater density of these surfactant ions to maintain constant potential. C. By accounting for the hydrophobic effect, the surfactants may associate and have increased adsorption. Constant potential is no longer a restriction. Charge and surfactant densities are schematic and not the result of calculation. Other counterions (e.g., H^+) not shown.

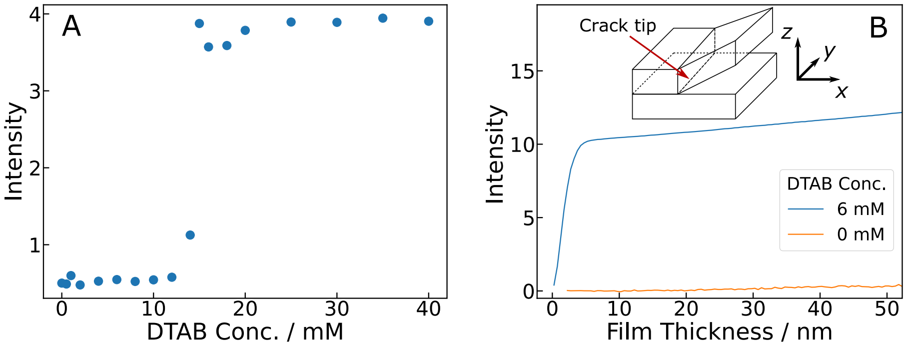

Fig. 2. Nile red fluorescence emission in arbitrary units. A. Fluorescence in aqueous solution as a function of DTAB concentration at pH 6. The fluorescence intensity of Nile red is very low below the cmc and very high above the cmc (14 mM). B. Fluorescence in the thin film between two glass wafers (a crack) as a function of film thickness. Nile red emission is negligible in the absence of surfactant and uniformly high in the presence of 6 mM DTAB. Inset is a schematic of the crack geometry and shows the coordinate system.

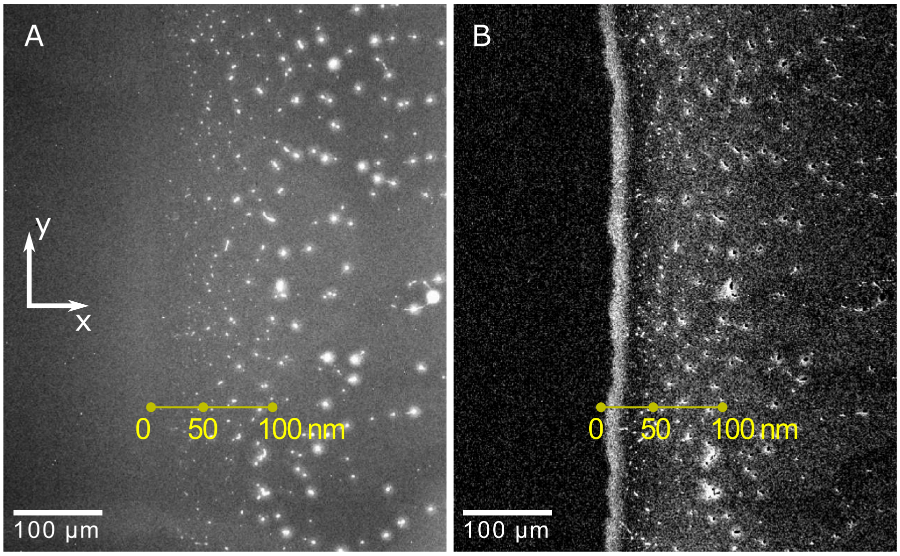

Fig. 3. Fluorescence Microscopy of thin aqueous film between glass surfaces. The film contains Nile red at pH 6.7. The crack is almost constant thickness in the *y*-direction and gently sloping in the *x*-direction such that for each 100 μm in *x*, the film is about 80 nm thicker, as shown by the yellow bar. (A) Nile red only in the solution. Fluorescent spots on this image suggests that there are some hydrophobic domains on the glass (contamination). (B) Difference Image between DTAB + Nile red and Nile red only. There is a clear fluorescence strip where the aqueous film is 0 to 30 nm thick. We interpret this as proximity-induced surfactant aggregation.

thermal bonding procedure; they were not observed on the single wafers before bonding. Nevertheless, these spots should not affect our experiment as their positions and sizes do not change with further addition of surfactants. After replacement of Nile red with a solution with DTAB plus Nile red, the region of small film thickness (near the crack tip) becomes fluorescent, but the remaining area does not. This is direct evidence of a hydrophobic domain that only forms when the two solids are close together. The fluorescent strip is shown in the difference image in Fig. 3B; by difference we mean the difference between the images with and without the DTAB. We have included on the figure a yellow bar showing the thickness of the aqueous film as a function of position. As shown in the figure, there is a clear bright fluorescent strip near the tip of the crack, where the thickness varies from about zero to 30 nm. We interpret this fluorescent strip as surfactant aggregation that only occurs where the two interfaces are close together, thereby providing the evidence for the main conclusion of this letter.

To provide better quantitation of the effect, we plot in Fig. 4 the intensity as a function of film thickness. Fig. 4 shows that the film is 0~30 nm thick in the region containing aggregates. A typical micelle is only about 3 nm thickness, so the micelles do not span the crack. The extended length of DTAB length is about 1.67 nm [27], so it is not one monolayer per surface or even two. It is likely a separate layer on each side of the crack as shown schematically in Fig. 1C. The 30 nm is not an indication of the thickness of the surfactant layer but a result of the range of the electrostatic force that drives adsorption and aggregation. The surfactant concentration is 0.10 mM, which corresponds to a Debye length of 30 nm. The aggregation occurs at a range of up to 30 nm

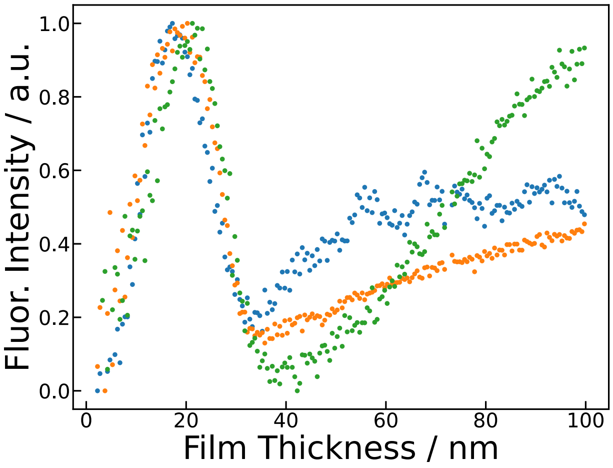

Fig. 4. Fluorescence intensity of Nile red as a function of film thickness in a glass crack containing 0.10 mM DTAB (well below the cmc). There is a peak of intensity from 0 nm to 30 nm, which we interpret as an aggregated surfactant layer on each glass surface. The gradual increase in intensity beyond the peak is an indication of the weak fluorescence of Nile red in bulk solution. Three independent experiments are shown. For each experiment, the image pixels were binned by film thickness and the data points are for bins of 0.5 nm width. This is similar to an average along the y direction.

because, at greater film thicknesses, the charge on one surface is too heavily screened by the solution to drive aggregation on a second surface.

The intensity of the fluorescence is lower for the proximity-induced aggregates below the critical surface aggregation concentration than for the surface aggregates at large separation above the critical surface aggregation concentration. This can be seen by comparing the noise in Fig. 2B to Fig. 4. Lower fluorescence is consistent with less Nile red or a less hydrophobic environment. For this reason, we have sketched hemimicelles rather than micelles in the cartoon shown in Fig. 1C.

We have demonstrated proximity-induced adsorption. From here, we describe additional experiments that are consistent with the claim that the origin of the effect is the interaction of the electrical potentials on the two surfaces. First, we decreased the magnitude of surface potential on each isolated surface by decreasing the solution pH. The negative solution potential on glass is obtained by the following dissociation: $-\mathrm{SiO{-}H} \rightleftharpoons \mathrm{SiO^-} + \mathrm{H^+}$; by decreasing the pH, we push this equilibrium to the left and discharge the silica–aqueous interface. When we reduced the pH from 6.7 to 3.5, we did not observe the bright strip at 0.10 mM DTAB. This could be from lowering the adsorption at large separation or by lowing the proximity-induced adsorption.

Second, given our hypothesis that the proximity-induced effect is caused by an electrostatic interaction between the surfaces (overlap of the diffuse double-layers), we repeated the measurement in a solution where the electrostatic interaction had a shorter range, i.e., with a shorter Debye screening length. We measured the effect of the addition of 0.10 mM NaBr that decreased the Debye length from 30 to 20 nm. As shown in Fig. 5, the addition of salt produced a reduced both the range of film thickness over which the fluorescence emission is observed and produced weaker emission. This is consistent with aggregation being induced by overlap of the diffuse double-layers. In summary, the effect of pH and salt addition are consistent with electrostatically driven proximal adsorption.

In conclusion, we have demonstrated that the aggregation of cationic surfactant in a thin film between two anionic surfaces is different than the surfactant aggregation in a thick film or indeed for an isolated solid–liquid interface. Below a film thickness of about one Debye length, the structure of cationic surfactant transforms from isolated molecules to aggregates, which supports the idea that the change in aggregation on one surface is driven by the overlap of the electrostatic double-layers from each interface. This shows that it is not valid to assume that surfactant structure is invariant with film thickness, and strongly suggests that it is unwise to treat charge regulation of surfaces in surfactant solution (or other complex ions) with no account of short-ranged hydrophobic or other interactions. It is well known that surfactant adsorption can lead to charge reversal, so the lower bound for double-layer forces between surfaces in surfactant solution is not constant potential, it is at least zero potential. As described previously, if correlations between mobile charges or charge patches are allowed, then the electrostatic interactions could be attractive [28–30].

Author statement

Zechen Zhang: Methodology, Software, Investigation, Data curation, Formal analysis, Writing - Original Draft, Writing - Review & Editing

Jared R. Arkfeld: Investigation

William Ducker. Supervision, Conceptualization, Methodology, Formal analysis, Writing - Review & Editing, Funding acquisition

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

William Ducker reports financial support was provided by National Science Foundation.

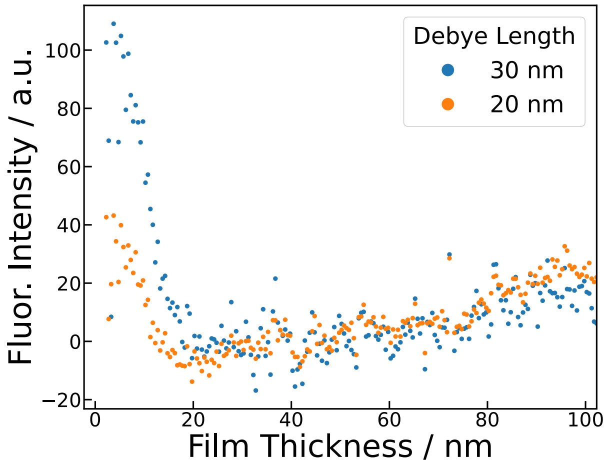

Fig. 5. Effect of 0.10 mM NaBr salt on fluorescence emission from Nile Red dye in DTAB surfactant solution in a thin film between glass surfaces. Addition of salt lowers the Debye length from 30 to 20 nm and also reduces the range and intensity of the fluorescence peak. Note that the data for Figs. 4 and 5 are for chips obtained from different wafers, and the thickness and intensity of the strip varied somewhat from wafer to wafer, which is understandable because each wafer would have a slightly different surface potential. In this case the bright strip was about 20 nm thick without the additional salt. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.colcom.2022.100657.

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