

Effects of Surfactants on the Formation and the Stability of Interfacial Nanobubbles

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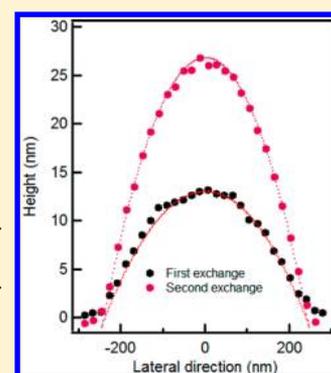
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S Supporting Information

ABSTRACT: Contamination has previously been invoked to explain the flat shape and the long lifetimes of interfacial nanobubbles (INBs). In this study, the effects of surfactants on the formation and the stability of INBs were investigated when surfactants were added to the system before, during, and after the standard solvent exchange procedure (SSEP) for the formation of INBs. The solutions of sodium dodecyl sulfate (SDS) above critical micelle concentration were found to have little effect on the bubble stability. Likewise, cleaning of the substrate with a surfactant solution had little effect. In contrast, addition of a water-insoluble surfactant during the formation dramatically reduced the INBs. Finally, repeated application of SSEP to surfactant-coated substrates progressively rinsed the surfactant off the system. Thus, we found no evidence to support the hypothesis that (1) INBs are stabilized by a layer of insoluble organic contaminant or that (2) SSEP introduces surface-active materials to the system that could stabilize INBs.



INTRODUCTION

Interfacial nanobubbles (INBs) are small gas bubbles present on a solid surface in water. They can influence various interfacial phenomena, such as surface interactions, slip boundary conditions, and adhesion of proteins and nanoparticles on surfaces.^{1–4} INBs usually have the shape of a lens with the height of several to several tens of nanometers and the lateral size of a few micrometers. Experimentally, it has been observed that the INBs can be formed under several circumstances: (1) by the entrainment of air pockets on a solid surface upon contact with water;^{5–7} (2) by application of appropriate temperature gradients;^{8–10} (3) by exposure of the solid surface to gas-saturated water by pressurization or electrochemical reaction;^{11,12} (4) by the exchange of a short-chain alcohol with water (the standard solvent exchange procedure; SSEP).^{8,13–18}

INBs can have a lifetime as long as several days.^{5,11,13,19} The long-term stability of INBs is surprising because of their small volume. The small volume means that diffusion distances are short and few gas molecules need to leave to eliminate the bubble. AFM measurements of the radii of curvature, r , of the air–water interface vary, but many of them are below about 10 μm and some are below 100 nm. The surface tension of pure water is about 72 mJ m^{-2} , so when compared to the surrounding solution, the bubbles should be under an additional pressure of at least 0.14 atm ($r = 10 \mu\text{m}$) and sometimes 14 atm ($r = 100 \text{nm}$), according to the Laplace equation. Spectroscopic evidence shows that the more gently

curved bubbles are close to one atmosphere in absolute pressure.^{19,20} Ljunggren and Eriksson have shown that the lifetime of curved bubbles is extremely short.²¹ The apparent clash between the observed stability and the predicted instability from the pressure has led to several hypotheses to explain the stability.^{3,10,22,23}

Lohse et al. proposed that gas comes into the INB to compensate for the diffusion out.^{24,25} That is, the INB is in a steady state. The problem with this hypothesis is that gas has to flow in and out of the same nanobubble, which requires an energy source, the origin of which is unclear. Also, such an energy source would need to maintain a gradient in the chemical potential of the gas molecules in the fluid outside the bubble (or inside the bubble) on a similar length-scale as the bubble. It is not clear how this gradient is maintained over such a small distance.

Contamination of bubble surfaces has long been used to explain the stability of bubbles that form during decompression sickness.^{26–28} Attard summarized three possible hypotheses for the long lifetime of INBs: one was that the presence of contaminants reduced the gas–water interfacial tension.²² Ducker also proposed that the presence of a water-insoluble surfactant on the interface could stabilize INBs.¹⁹ If the surfactant were localized at the gas–water interface, then as gas

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leaked out of the bubble, the surfactant would become more concentrated and diminish the surface tension with concomitant reductions in the Laplace pressure across the interface. A large reduction in surface tension should produce improved stability. Thus, the observed stable bubbles could be the highly contaminated remnant of larger area bubbles that had a lower density of contamination. The use of an organic solvent during the standard solvent exchange procedure (SSEP) was of particular concern because the organic solvent could dissolve and carry a wide range of chemicals to the bubble. Insoluble contaminants could be swept from the solid–liquid interface as it advances across the solid, or adsorb via diffusion from the solution. This hypothesis was supported by the observation that INBs apparently disappeared when water was replaced with a micellar surfactant solution. The micelles were designed to remove and solubilize the pinned contaminants, and the disappearance of the bubbles was explained in terms of the loss of the stabilizing molecules from their surface.²³

As all the experimental studies of INBs have been carried out in air, it is almost unavoidable that the gas–water interface adsorbs some impurities. There are some hints which might be interpreted as the presence of some kind of ‘skin’ on INBs. For example, INBs could be moved around on the surface by a scanning AFM tip.²⁹ On the other hand, the Ostwald ripening observed between differently sized INBs and disappearance of carbon dioxide INBs with time suggested that the INBs were most likely permeable to gas. The question thus remains open: to what extent do the surface-active impurities influence the formation and stability of INBs?

In this work, we examine how surface-active compounds influence the formation and stability of INBs. We specifically add surfactants into the system before, during, and after the INB formation. We find that the addition of surfactants did not facilitate the formation of INBs or remove INBs that have already been formed at the interface. Rather than introducing surface-active contaminants to the system, our results suggest that sequential SSEP rinses adsorbed surfactants off the surface.

MATERIALS AND METHODS

1. Substrates and Chemicals. Highly oriented pyrolytic graphite (HOPG) (ZYB, SPI) was freshly cleaved immediately before use as the substrate. We previously used several different hydrophobic surfaces as the substrate for the study of INBs but chose HOPG in this work because (1) HOPG was used in Ducker’s early study, (2) formation of INBs is highly reproducible on HOPG, and (3) HOPG has been widely used by various research groups. Water used in the study was from Milli-Q unit (Millipore, 18.2 M Ω resistivity). Ethanol was double-distilled in air before use. Water, distilled ethanol, and aqueous solutions under study were stored in partially filled and sealed glass bottles inside a refrigerator (4 °C) overnight to be equilibrated with the air. The water and aqueous solutions were slowly (for 20 mL of water over 20 min) warmed up to ~30 °C just before use, and the ethanol at 4 °C was used without warming. All of the glassware was cleaned with 10% NaOH solution and rinsed thoroughly with a large quantity of water. All the tubing used for the solvent transport was made of Teflon. Sodium dodecyl sulfate (SDS, >99% Sigma Aldrich, critical micelle concentration (cmc): 7 mM) was used as received. Cetyltrimethylammonium bromide (C₁₆TAB, Sigma Aldrich, cmc: 0.9 mM) was recrystallized in acetone and ethanol before use. Oleic acid (CH₃(CH₂)₇CH=CH(CH₂)₇COOH, >99%) was received from Sigma-Aldrich and used without purification.

2. Formation and Characterization of INBs. INBs were produced by SSEP. The details of SSEP are documented in our previous work.^{13,14,19} In brief, the substrate was exposed to ethanol in a closed AFM fluid cell in stage 1. Then water was gently injected into

the cell to replace ethanol in stage 2. INBs were produced after the exchange of ethanol by water. The INBs were imaged by tapping mode atomic force microscopy (TM AFM) (Multimode IV, Bruker) in liquid with the closed fluid cell. Silicon nitride cantilevers (NP, Bruker) were cleaned for 15 min in UV/ozone cleaner (ProCleaner Plus, Bioforce Nanoscience, Inc.) before use. The contact angle of INBs was deduced from the cross-sectional profiles of INBs in the AFM images by a MATLAB program. The same types of AFM tip and imaging parameters were used in each experiment to minimize systematic errors in the morphology of INBs.

3. Light Scattering. Static light scattering (SLS) offers a sensitive measure of the presence of particulate or insoluble impurities in the solution. Light scattering was measured using a high performance particle sizer (Malvern). The measurement of each sample was carried out for 3 runs and 10 measurements in each run with the same intensity of laser. Scattering intensity in kilo counts per second (kcps) was recorded for the samples.

During SSEP, 6 mL of distilled ethanol was injected into the AFM fluid cell from the entrance port. As the volume of the fluid cell (~0.5 mL) is smaller than 6 mL, the majority of the ethanol passed through the AFM fluid cell and out of the exit port. The ethanol from the exit port was collected in three separate vials, each containing ~2 mL, and labeled as the first, second, and third 2 mL. Then ~6 mL of water was injected into the fluid cell to replace the ethanol left in the fluid cell (~0.5 mL). The dilute ethanol solution (0.5 mL ethanol + ~5.5 mL water) which came out of the exit port was also collected and measured by the light scattering (labeled as “exchange”). The light scattering intensity of the ethanol and that of water were also measured for comparison.

RESULTS

1. INBs after Exposure to Micellar Surfactant Solutions. It was difficult to obtain highly reliable AFM images of INBs in a surfactant concentration near or above the cmc because the diminished surface tension of the gas–water interface meant that a larger deformation of the INB occurred by the AFM tip.³⁰ To enable more careful imaging of the surface after cleaning with the surfactant, we replaced the surfactant solution with water and then imaged the interface. Such a procedure necessitated a control to see whether the exchange of 5 \times cmc SDS for water produced INBs. The result showed that INBs were not formed by exchanging 5 \times cmc SDS for water.

The first experiment was to examine whether the putative stabilizing contamination of the gas–water interface could be removed by washing INBs with a micellar surfactant solution. This followed the work by Ducker where the INBs on HOPG had been destabilized by exposure to a 5 \times cmc SDS solution.²³ Figure 1 shows two series of images of the graphite surfaces after the surfaces were exposed to ethanol, water (stage A), 5 \times cmc SDS (15–30 min, stage B), and then water (stage C). The flow rate of the fluids during stages B and C must be kept low (approximately 3 s for 0.25 mL) to preserve the INBs that had been formed on HOPG at stage A. Series 1 had INBs with micropancakes, and Series 2 had INBs only. The important conclusion is that after rinsing with micellar SDS solutions, and then with water (to improve the ability to image), the nanobubbles and micropancakes remained.

Similar results were observed when cationic or nonionic surfactant was used in place of SDS. INBs remained after the exposure to 5 \times cmc C₁₂TAB or C₁₂EO₈ solution. As micellar surfactant solutions are known to remove organic contaminants from the gas–water interface, yet the INBs remained after rinsing with micellar solutions, these results do not support the hypothesis that contaminants stabilize INBs.

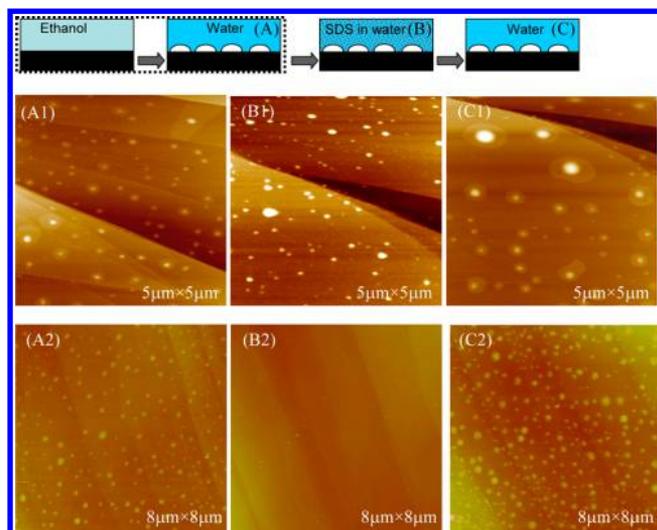


Figure 1. Stability of INBs in surfactant solution above CMC on two HOPG surfaces (1 and 2). INBs in water after SSEP (stage A, AFM images: A1 and A2), in $5 \times$ cmc SDS solution (stage B, AFM images: B1 and B2) and then in water again (stage C, AFM images: C1 and C2). Both INBs and micropancakes were detected on surface 1 while only INBs were detected on surface 2. Both of these features remained after the exposure to $5 \times$ cmc SDS solution, although the number density of micropancakes diminished somewhat after the exposure. The solution in which AFM images were recorded is indicated in the schematic drawing.

We note that the replacement of the surfactant solution with water must be carried out carefully so as not to form any large bubbles in the AFM cell. We observed only bare substrate when a big bubble swirled through the fluid cell during the injection of the liquid. The interference from big bubbles might be the reason why INBs were not observed after the exposure to the $5 \times$ cmc SDS solution in the earlier work.²³

2. Influence of Insoluble Surfactants during SSEP. In this series of experiments, a model contaminant was added into ethanol and/or water before the exchange, in an effort to mimic the presence of insoluble surface-active contaminants during SSEP. Oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$) was chosen as the model contaminant because it is insoluble in water and has been shown to hinder the gas diffusion from bubbles.³¹ The SSEP was performed using a 1 mM solution of oleic acid in ethanol and then pure water. The exchange could not reproducibly form INBs: only one out of eight experiments produced INBs, as shown in Supporting Information Figure 1. Thus, the presence of a water-insoluble surfactant (oleic acid) in the ethanol actually hinders rather than enhances the formation of INBs. This may be because the oleic acid could coat the graphite and make it hydrophilic.

3. Formation of INBs with Soluble Surfactant Solution Instead of Water. The aim of this section is to understand how the formation of INBs is affected by surface-active impurities in water. The solvent exchange procedure was performed but instead of following ethanol with water, the ethanol was followed with SDS solution. Figure 2 shows that no INBs were detected with SDS solution of $1 \times$ cmc whereas some INBs were detected with $0.2 \times$ cmc SDS solution. We note that the surface excess of SDS on graphite in $0.2 \times$ cmc solution is only about half of the surface excess at the cmc.³² When cationic surfactant (C_{16}TAB) solution of $0.2 \times$ or $0.8 \times$ cmc was used in the place of $0.2 \times$ cmc SDS solution, some

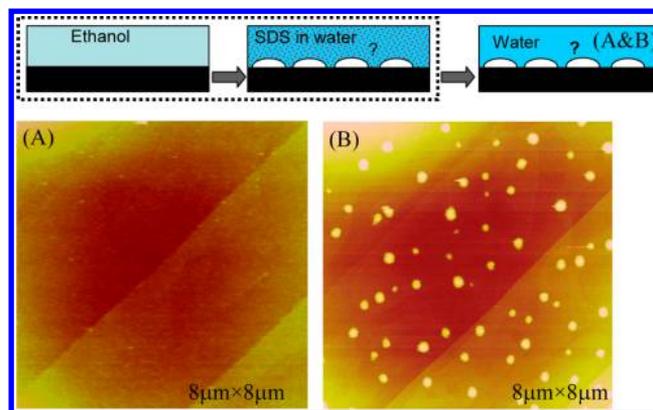


Figure 2. SSEP with soluble-surfactant solution in the place of water. (A) AFM image of a freshly cleaved HOPG substrate after it was exposed to the sequence of ethanol, $1 \times$ cmc SDS solution, and then water. No INBs were observed in water. (B) AFM image of a freshly cleaved HOPG substrate after it was exposed to the sequence of ethanol, $0.2 \times$ cmc SDS solution, and water. INBs were observed in water.

INBs were also formed, similar to $0.2 \times$ cmc SDS solution. The above results show that the formation of INBs was not facilitated by the presence of soluble surfactant in the water during the solvent exchange. Instead when the amount of surfactant in water was above the cmc, the surfactant hindered the formation of INBs. We explain this result in terms of the graphite interface becoming hydrophilic in the presence of cmc surfactant: bubbles do not attach or form at a hydrophilic interface. Similar results were recently reported for a CTAB-coated surface.³³

We also examined the formation of INBs on octadecyltrichlorosilane (OTS)–silicon surfaces: INBs were not detected after the sequence of ethanol, $0.2 \times$ cmc SDS solution, and then water. Multiple applications of SSEP were necessary before INBs could be detected, regardless of the presence of surfactants. This shows that INBs on OTS–Si were not facilitated by the presence of soluble surfactants in water. Unfortunately, we could not provide quantitative comparison of the number density or the size distribution of INBs formed with or without surfactant, because these parameters varied in a large range under apparently identical experimental conditions for the OTS–silicon system.

4. Cleaning Effect of SSEP. It has been suspected that SSEP can lead to the contamination of the solid–liquid interface because organic solvent could transport a wide range of chemicals to the interface. Here we show that SSEP can actually clean the solid–liquid interface. We use the contact angle of INBs (measured through the gas phase) to infer the cleanliness of the interface. A greater angle is consistent with less surface-active contaminant.

In the first type of experiments, we formed INBs by SSEP on a freshly cleaved HOPG shown in Figure 3A. We then exposed the surface to $0.8 \times$ cmc SDS solution for 0.5 h and carried out another SSEP to the surface. INBs were observed as shown in Figure 3B, in the same imaging area as in Figure 3A. Importantly, the size and the number density of the INBs were similar. The cross-sectional profile of INBs was fit to a spherical-cap shape, from which the contact angle of INBs was deduced. The plot of the contact angle versus the height showed a trend similar to INBs produced by SSEP on freshly cleaved HOPG (Figure 5C), suggesting that the exposure of

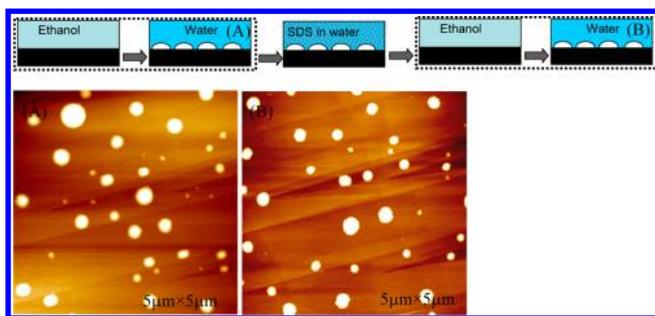


Figure 3. Formation of INBs by SSEP on the surface that had been exposed to a surfactant solution. A freshly cleaved HOPG surface was exposed to the sequence of ethanol, water (A), $0.8 \times \text{cmc}$ SDS solution, ethanol, and water again (B). INBs were detected in both water (A) and water (B), showing that SSEP can induce INBs on both freshly cleaved HOPG (A) and surfactant-exposed HOPG (B) surfaces.

substrate to up to $0.8 \times \text{cmc}$ SDS did not make any significant difference to the formation or the morphology of INBs after SSEP.

In the second type of experiments, a small droplet of the $0.8 \times \text{cmc}$ C16TAB solution was deposited on the freshly cleaved HOPG. The droplet was left on the surface for several minutes to allow adsorption of the surfactants to the surface, and then the droplet was spun off the substrate. The surface was gently rinsed with ethanol, dried with stream of nitrogen gas, and used as the substrate. Multiple SSEPs were carried out on this surfactant-coated surface, and the surface was imaged in water after each SSEP. The AFM images in Figure 4 shows that the

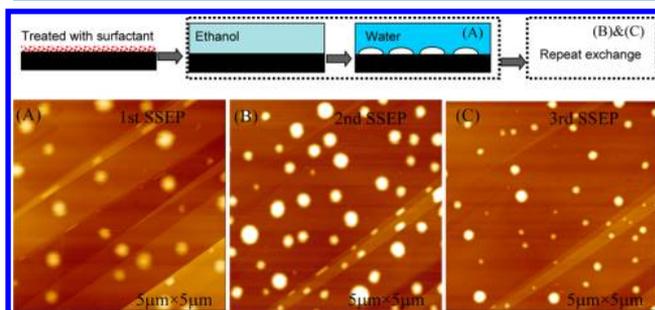


Figure 4. Effects of preadsorbed surfactant on the formation of INBs by SSEP. A freshly cleaved HOPG was doped with a droplet of $0.8 \times \text{cmc}$ C16TAB, rinsed with ethanol, and then dried with a flow of nitrogen gas. Then the surfactant-coated HOPG was subjected to a series of SSEP. AFM image in water after the first SSEP (A), after the second SSEP (B), and after the third SSEP (C).

size and the number density of INBs were not dramatically different from those generated by SSEP on a freshly cleaved HOPG substrate. However, the contact angle of the INBs after the first SSEP on the surfactant-treated HOPG was significantly lower than that after the second SSEP (Figure 5). After the second (and subsequent) SSEP, the contact angle approached an asymptotic value that was similar to that on a freshly cleaved HOPG. We note that all the images used for the morphology analysis in Figures 4 and 5 were recorded using the same AFM tip.

These results clearly show that SSEP did not lead to more contaminated system, which is opposite to the suspicions in the literature.^{23,34} Contrary to the suspicions, sequential SSEP had progressively rinsed off the preadsorbed C16TAB on the

HOPG. Recent work also showed that nanoparticles deposited on a surface were washed off the surfaces after SSEP,³⁵ consistent with the cleaning effect from SSEP observed here.

5. Light Scattering from the Exchange Solutions. We further characterize SSEP by measuring the scattering intensity of the liquids at different stages of SSEP using SLS. This technique is very sensitive to particulate or water-insoluble impurities. In previous work, it was found that compared to scattering of ~ 20 – 30 kilo counts per second (kcps) from the double-distilled ethanol in water, the scattering intensity of the mixture of (as received) analytic grade ethanol and water could increase by 1 order of magnitude (200 kcps). Presence of 5–10 ppm decane in ethanol could increase the scattering intensity of 20% ethanol aqueous solution by 2 orders of magnitude.³⁶

Compared to the scattering intensity of freshly distilled ethanol (~ 30 kcps), the first 2 mL of ethanol that came out of the exit port of the fluid cell during SSEP had a significantly higher scattering intensity of 170 kcps, as shown in Figure 6. The second and third 2 mL of ethanol, in contrast, showed a level of scattering intensity similar to that of the distilled ethanol control. We assume that the higher intensity of the first ~ 2 mL of ethanol was caused by the flow of ethanol removing and carrying small, loosely attached graphite flakes from the HOPG substrate. Although the chemical nature of the significantly higher scattering intensity from the first 2 mL of ethanol is unknown, it has been effectively removed by the third 2 mL of ethanol. This shows that the SSEP could effectively eliminate the source of the scatter. After the injection of water, the scattering intensity of the outcoming dilute solution (0.5 mL ethanol and 5.5 mL water) was only slightly higher than that of pure water or ethanol.

After the AFM images of INBs were recorded, the AFM cantilevers were taken out from the fluid cell and dried in a laminar flow cabinet. The AFM image of INBs formed by SSEP and the SEM image of the cantilever are shown in Supporting Information Figure 2. Again no obvious contamination was found on the cantilever, consistent with the smooth clean tips shown by Borkent et al.³⁷

DISCUSSION

1. Surface-Active Contaminants Cannot Account for the Stability of INBs.

It is very difficult to study INBs in a strictly contamination-free environment during AFM measurements. However, from our results on the stability of INBs in surfactant solutions above the cmc, we consider it as highly unlikely that a heavily contaminated interface or an impermeable (polymeric or gel-like) gas–water ‘skin’ contaminants is the source of long lifetimes of INBs. First, if a minute amount of such impermeable ‘skin’ had existed in the system, a concentrated surfactant solution would have washed it away by the detergency action. Consequently INBs would have disappeared after the exposure to $5 \times \text{cmc}$ SDS solutions, which is contrary to our findings. Second, no obvious insoluble contaminants were detected from the light scattering of the solution from SSEP. Finally, we note that the dissolution of CO_2 INBs with time, the Ostwald ripening between INBs with time,¹¹ and growth of INBs after sonication or reduced pressure^{29,38} all indicate that the surface of the INBs was certainly ‘permeable’ to gas. We may conclude this section by stating that ‘impermeable skin’ is unlikely to account for the formation or the long-term stability of INBs.

2. Formation and Stability of INBs in Surfactant Solutions.

Our results show that INBs were not produced

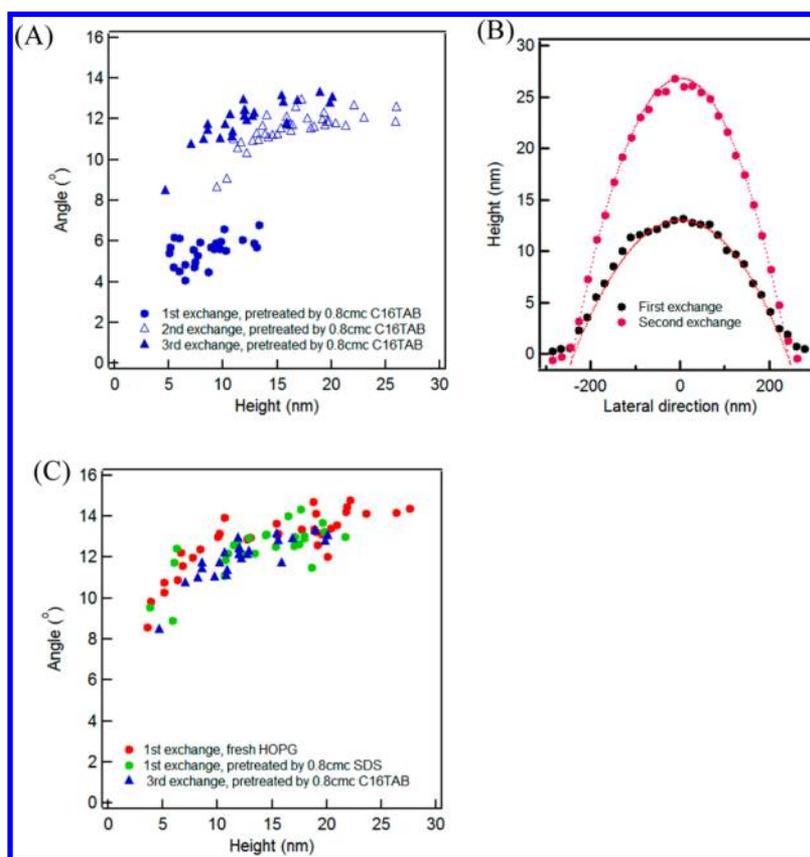


Figure 5. Morphology of INBs on C16TAB-coated HOPG substrates shown in Figure 4. Evolution of the contact angle of INBs on the surfactant-coated HOPG is shown with the number of applications of SSEP (A). The contact angle was measured through the gas phase. The data are shown for a large number of INBs that have significant size (height) distribution. Typical cross-sectional profiles of INBs after the first and the second SSEP on a C16TAB-coated HOPG are shown (B). The contact angle of INBs on C16TAB-coated HOPG after the third SSEP was compared to that on a freshly cleaved HOPG (C). Here the contact angle of INBs on the SDS-exposed HOPG (Figure 3, water B) after the first SSEP is also shown for comparison, which did not differ significantly from that on freshly cleaved HOPG even after the first SSEP.

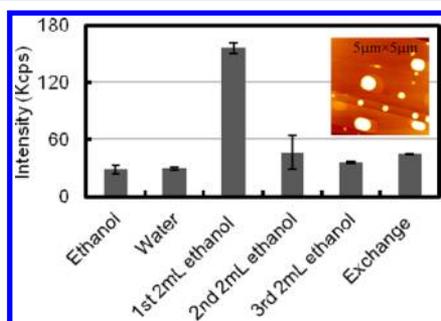


Figure 6. Light scattering intensity of the fluids used for SSEP. The scattering intensity of the first 2 mL of ethanol during SSEP is much greater than that of ethanol or water. The scattering intensity of the second and the third 2 mL of ethanol was much smaller than that of the first 2 mL but similar to that of water that was collected during the SSEP. The SSEP-induced INBs are also shown in the inset (the AFM image was recorded in water).

when ethanol was directly replaced by a concentrated (above cmc) surfactant solution in the place of water during SSEP. A plausible explanation for this result is that the wetting properties of the second liquid during SSEP determine the nucleation and the attachment probability of the INBs. A concentrated surfactant solution could wet HOPG as well as ethanol, which would prevent build up of sufficient amount of gas saturation in the vicinity of HOPG, the likely mechanism of

SSEP we outlined earlier.^{14,18} In addition, the presence of micelles in the aqueous phase could act as “sinks” for gases which could pre-empt the build up of supersaturation of the gas by SSEP.

Once INBs were formed on the surface, our results show that a $5 \times$ cmc surfactant solution did not wash INBs away from the surface. This could be due to two competitive effects on the stability of INBs. The gas–liquid surface tension of INBs was decreased by the presence of the surfactant, which could reduce the Laplace pressure inside the INBs and extend the lifetime of INBs. On the other hand, a surfactant solution appeared to relax (depin) the three-phase line of the INBs (we previously showed that exposure of irregularly shaped INBs to a surfactant solution made the boundaries circular).¹⁸ In short, the three-phase line becomes more mobile in the presence of surfactants. The principle of detergency is that surfactants facilitate breakaway of hydrophobic entities from a surface when combined with mechanical agitation. Thus INBs might still adhere on the substrate in the presence of surfactants but may detach with mechanical disturbance or a shear flow during injection of liquids. Our observation indeed showed that when a big bubble had perturbed the system during the replacement of SDS solution with water, no INB could be detected in water anymore.

CONCLUSIONS

INBs remained stable after the exposure to a surfactant solution of SDS that contained micelles ($5 \times \text{cmc}$) that should be able to solubilize many organic materials at the gas–water interface. This stability in the presence of micellar solutions does not support the hypothesis that INBs are stabilized by water-insoluble materials adsorbed at their gas–liquid interface.²¹ When the HOPG was rinsed with surfactant solution with the aim of cleaning the surface, INBs still formed at the surface after SSEP. This does not support the hypothesis that contamination originating from HOPG stabilizes INBs. When surfactants were adsorbed onto the solid before SSEP, the morphology of the bubbles was slightly altered. However, after repeated application of SSEP, the morphology of the bubbles became similar to that of INBs formed on freshly cleaved HOPG. This demonstrates that the surfactants preadsorbed on the surface can be progressively rinsed off with the application of SSEP. The addition of a water-insoluble surfactant, oleic acid, to the ethanol used during SSEP reduces the number of INBs. With the presence of water-soluble surfactants above cmc in water during SSEP, no INBs could be produced on HOPG. We conclude that, by adsorption to the graphite–liquid interface, surfactants reduce the hydrophobicity of the solid, thereby increasing the barrier to adsorption of the bubble and decreasing the stability of an adsorbed bubble.

ASSOCIATED CONTENT

Supporting Information

Effect of insoluble surfactant on the formation of INBs and SEM images of the AFM tip. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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