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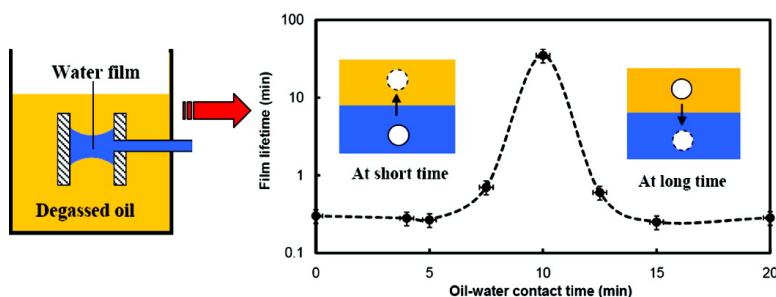**74** PUBLICATIONS   **577** CITATIONS

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Do Liquid Films Rupture due to the So-Called Hydrophobic Force or Migration of Dissolved Gases?

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Liquid films between hydrophobic (water-repellent) interfaces are not stable. The film rupture has been attributed to the so-called hydrophobic attraction. In this paper microinterferometry experiments show that gases inherently dissolved in water have a significant effect on the film rupture. Specifically, films of ultrapure deionized water in contact with degassed oil (squalene) were stable for as long as 35 min, while the water films in contact with nondegassed oil had a lifetime of seconds. These films ruptured at film thicknesses of ~150 nm. The degassed oil was also purposely left in contact with air. The oil-in-water emulsion films formed between degassed oil left in contact with air for a long period of time did not last longer than a few seconds and ruptured at significantly high thicknesses (about 800 nm). The degassing effect did not change the interfacial potential (about −65 mV) and the electrical double-layer repulsion between the squalene−water interfaces. Migration of dissolved gases between oil and water caused the rupture phenomena observed.

1. Introduction

Liquid films are of paramount importance in a wide range of applications, ranging from foam and emulsion productions in the pharmaceutical and food industries[1,2] to controlling bubble−particle interactions in the recovery of gold, diamond, and many other valuable minerals by flotation.[3−7] Improved understanding of the drainage, stability, and rupture of liquid films is profoundly important in these applications and has attracted numerous studies.[8,9] Principally, the film behavior is determined by two processes, thinning and breaking. Thinning of a film occurs by the draining of the liquid under the influence of gravity and/or capillary suction at the film periphery (and the Plateau borders). When the thickness is reduced to about 200 nm, intermolecular and surface forces influence the film drainage. For liquid films between two gas bubbles or two oil droplets, the double-layer repulsion decreases the draining rate, while the van der Waals attraction increases it. On further thinning the films normally become unstable and break at a characteristic critical thickness which is typically within the range from 10 to 200 nm, depending on the surfactant concentration.[10,11]

A number of theories have been suggested to explain the film rupture and to predict the critical thickness.[12−16] The early theory was proposed by de Vries and was developed in subsequent studies. These theories suggest that the film rupture is due to the growth of thermal-capillary waves on the film interfaces that are amplified by the attractive van der Waals force which rapidly increases with decreasing film thickness. The critical thickness can be predicted by a stability analysis of small amplitude thermal corrugations on thin films by introducing approximations for film thickness and (disjoining) pressure of surface forces in the hydrodynamic equations (the lubrication approximation) describing film drainage and corrugation growth. The new models for film rupture consider the essential physicochemical and hydrodynamic factors and agree with the available experimental data.[13,14,16]

The prerequisite for film rupture is the existence of attractive surface forces between the film surfaces. For foam films between two gas bubbles the attractive force is usually assigned to the van der Waals force. In the case of wetting films, the van der Waals force is repulsive and the electrical double-layer interaction can be changed to attraction by recharging the solid surface, for instance, by adsorbing multivalent ions onto a silica surface.[17] Without the surface modification, the Derjaguin−Landau−Verwey−Overbeek (DLVO) forces for the wetting films between an air bubble and a silica surface in water are repulsive and the films are stable. If the surface treatment is done by a hydrophobization process with a hydrophobizing reagent, such as methylation[18] or esterification,[19] the wetting films on such hydrophobic surfaces are not stable and normally rupture quickly. The rupture of films between hydrophobic surfaces has been explained by postulating the existence of a long-range hydrophobic attraction of molecular nature[20] which is due to, for

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example, the restructuring of water molecules at the hydrophobic surfaces.[21,22] However, the measured attractive force between hydrophobic solid surfaces in water shows that the "truly hydrophobic" force due to the water restructuring at hydrophobic surfaces is short-ranged (<10 nm) and that there exists a longer ranged force (>10 nm) due to mechanisms unrelated or only indirectly related to the surface hydrophobicity.[23-26] One popular proposed mechanisms is the nanobubble bridging which asserts that the long-ranged hydrophobic attractive force is due to the coalescence of pre-existing sub-microscopic bubbles adhering to the hydrophobic surfaces that bridge the two approaching hydrophobic surfaces.[23-26] The pre-existing sub-microscopic bubbles adhering to the hydrophobic surfaces can be formed by repeatedly contacting and separating the solid surfaces which is a routine experimental procedure of measuring forces with atomic force microscopy using the colloidal probe technique.[27] Indeed, no long-ranged attraction was measured if the hydrophobic surface was not previously contacted.[28] While the nanobubble bridging is important in explaining the attraction between hydrophobic solid surfaces in water, it cannot explain the long-ranged attraction between gas bubbles in dilute surfactant solutions[11,29] and the rupture of foam films because the macroscopic (hydrophobic) bubbles would instantly coalesce (in dilute surfactant solutions) and, therefore, the pre-existing sub-microscopic bubbles cannot be formed at (and cannot adhere to) the air−water hydrophobic surfaces by repeatedly contacting and separating the air−water surfaces.

The important role of nanobubbles in the rupture of wetting films has also been considered.[17] The film rupture by nanobubbles has been explained by a number of steps. First, during the film drainage the apex of the largest nanobubbles on the solid hydrophobic surface comes closer to the surface of the macroscopic bubble where surface forces are acting. Therefore, an aqueous foam film of nanometer size is effectively formed between the macroscopic bubble and the nanobubble, where the van der Waals interaction is attractive. The attractive van der Waals force can destabilize the film locally. The concave surface of the nanobubble can also increase the local capillary pressure significantly, which can be an important additional factor of the local film destabilization. If the local film destabilization forms a hole with a diameter larger than the critical diameter (∼10 nm),[6] the entire wetting film is destabilized and the hydrophobic surface becomes dewetted. This proposal for the wetting film rupture by nanobubble is referred to as the nucleation mechanism and has been supported by the direct imaging of nanobubbles at hydrophobic surfaces in water by atomic force microscopy.[19,24,30-33] However, the imaging of nanobubbles by atomic force microscopy (AFM) tapping mode normally requires surface

treatment with liquids supersaturated by air or gases, usually by rapid temperature change or alcohol−water exchange. The treatment by alcohol−water exchange involves flushing liquids through the AFM fluid cell in the following consecutive steps: water−ethanol−water.[19] These required surface treatments have not been applied to the preparation of the solid surfaces used in the experiments of the wetting film rupture. Therefore, the nanobubble proposal for the film rupture remains questionable despite ample evidence supporting the existence of nanobubbles at the hydrophobic surface−water interface.

In this paper we present direct experimental evidence of the important role of air inherently dissolved in water in liquid film rupture. In particular, we have developed and used a special experimental setup and procedure to show the critical effect of the migration of dissolved gases on the drainage and rupture of water films between two hydrophobic oil−water interfaces.

2. Experimental Section

2.1. New Experimental Approach. The drainage and rupture of liquid films have commonly been studied using microinterferometry developed by Scheludko[12] using the Scheludko cell. Briefly, microscopic films of radius from 0.05 to 0.2 mm can be formed between the tips of the menisci of a biconcave drop held in a cylindrical glass tube (of 2.0 mm radius) by sucking the liquids out of the tube (Figure 1). The film holder is normally placed in a measuring glass cell with controlled environment and enclosed in a water jacket which is maintained at a constant room temperature (±0.1 °C). The amount of liquid in the biconcave drop is controlled by a gastight syringe by which the film radius can be varied.

The water films in the Scheludko cell can principally be degassed to examine the effect of nanobubbles and dissolved gases on film rupture. However, the degassing of water films which are in direct contact with air, such as in the wetting films or in foam films, is ineffective. As a result, oil-in-water emulsion films have been used. The in situ degassing of the emulsion film inside the Scheludko cell still suffers from many technical complications, such as mechanical vibration and instability or fracture of fine glass cells, which make the problem unsolvable if the conventional degassing by applied vacuum is followed. Indeed, we solved the problem with a new idea. The underlying principal is that since the solubility of gases in oil is approximately 10-fold higher than that in water, once the oil is separately degassed, its contact with a small amount of water, which normally contained dissolved gases from air, can initiate a transfer of gases from the water toward the oil and degas the water. We have also discovered that the migration of dissolved gases from the water into the oil phase and the reverse process have quite different effects on the film rupture. The experimental details are described as follows.

2.2. Materials. Deionized (DI) water used was produced from tap water purified by an RO system and a Milli-Q Academic System (Millipore, Billerica, MA). The resistivity of the water remained at 18.2 MΩ and its total dissolved organic content was less than 10 ppb. The oil used was squalene (Sigma Aldrich, St. Louis, MO), which is a highly unsaturated hydrocarbon ($C_{30}H_{50}$) and contains large amounts of dissolved gases. (Concentration of air soluble in oil is about 10 times higher than that in water.) Squalene was used as purchased. Precautions were taken to exclude possible oxidation and cross-linking in squalene. The oil was degassed by repeated removals of dissolved gases using a vacuum diaphragm pump (MD1, Vacuubrand Inc., Essex, CT) with an ultimate total pressure of 1.5 mbar. A 40 kHz ultrasonic bath and a Teflon bar placed at the bottom of the glass cell containing the oil were also used to enhance the removal of dissolved gases. The hydrophobic Teflon bar served as a nucleation center for the formation of dissolved gas bubbles and significantly increases, in conjunction with mixing the oil in the ultrasonic bath, the efficiency of the degassing procedure by the vacuum pump. The pump worked continuously. The ultrasonic bath worked with separate sessions of 10 min with a few minutes pause between sessions. During the first 10 min the oil vigorously released gas bubbles. Then the speed of the releasing bubbles reduced. After

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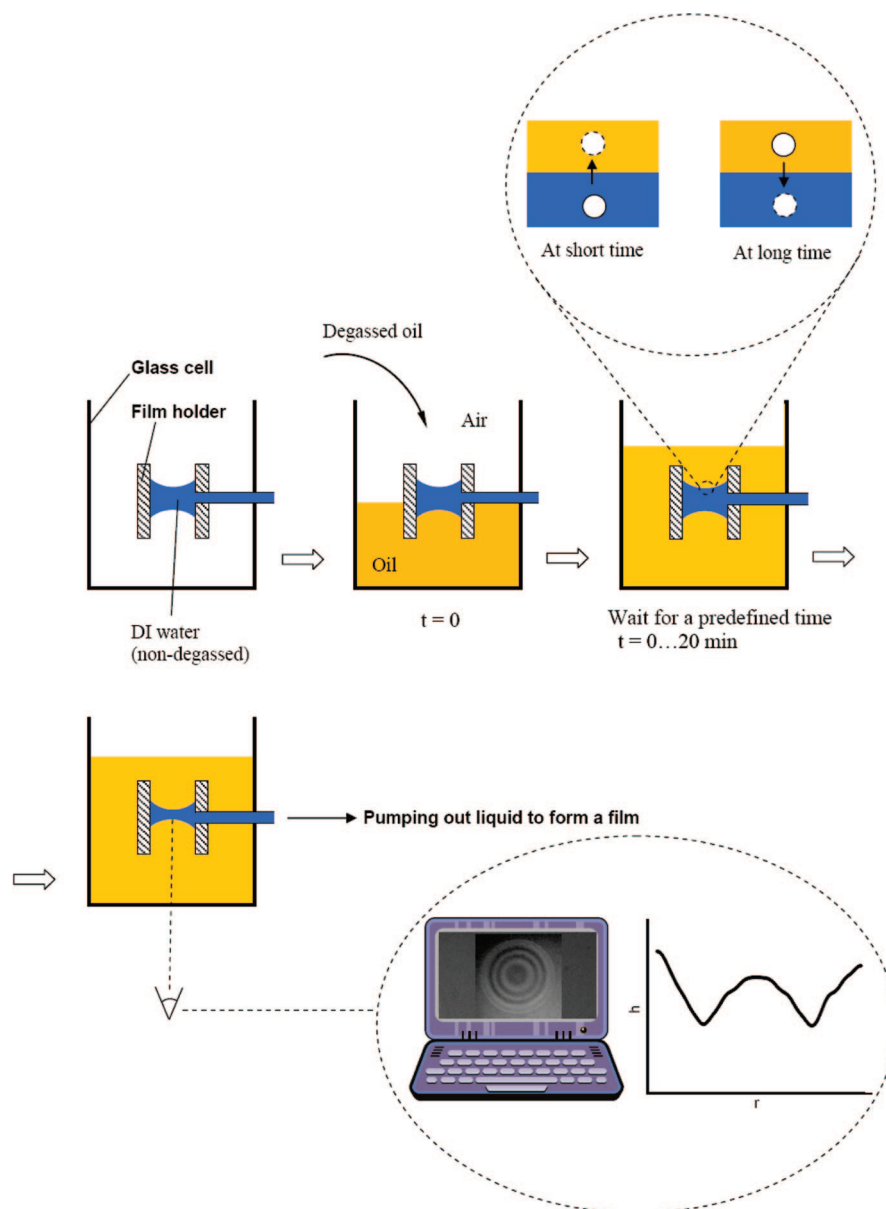
Figure 1. Schematic representation (not to scale) of the experimental method and procedure using the Scheludko cell and the thin film balance to study the effect of degassing on the drainage and stability of thin films between hydrophobic oil−water interfaces.

approximately 3 h no bubbles were generated and the degassing procedure was stopped. The degassed oil was immediately transferred into the Scheludko cell for the experiments with liquid films.

All the glassware and the Scheludko cell were thoroughly cleaned by soaking in a freshly prepared RCA SC-1 solution developed by Kern and Puotinen[34,35] and sequentially rinsed with a large quantity of deionized water. The cleanliness of the Scheludko cell and the DI water was checked by a water purity test: The system was clean if no water film could be formed and registered with the Scheludko cell within a second fraction; otherwise, the system (the Scheludko cell and the DI water) was contaminated, and the cleaning procedure and the purity test had to be repeated until no water film was observed.

2.3. Methods and Procedures. The effect of degassing on the drainage and stability of the thin oil-in-water emulsion films were investigated using the thin film balance (TFB) of Scheludko.[12,36] First, a droplet of the DI water was formed inside the film holder

of the Scheludko cell and immersed in the freshly degassed squalene for about 5, 10, 15, and 20 min (Figure 1). The moment when the water and the freshly degassed oil were brought into contact was referred to as zero time ($t = 0$). For each of the experiments the same amount of the DI water was placed into the film holder. Since the water was not degassed, dissolved gases in water were expected to migrate into the degassed oil. After the predefined contact time between the DI water and the degassed oil, the water was carefully pumped out using a gastight nanoliter syringe pump to form a water film between the oil−water interfaces. The film formation, drainage, and rupture were observed through an inverted microscope (Nikon, Tokyo, Japan). White light from a 100 W source was perpendicularly incident on the film surface at its center. The film was observed in reflected light through a calibrated eyepiece and the film radius was determined with an accuracy ±0.005 mm. Precautions were taken to eliminate the effect of external disturbances, such as vibrations, on the film thinning process as well as the film rupture.

The interferograms produced by the phase shift of the light reflection from the two film surfaces were recorded by a digital camera system (PowerShot A640, Canon, USA) and stored in a

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computer for further off-line analysis and processing to determine the film lifetime and the film thickness versus time employing a digital filtration procedure.[36]

The film thickness, h, at any instance of time was estimated from the intensity of the monochromatic light (digitally filtered) using the Scheludko inteferometric equation, which accounts for the light interference by multiple reflections by both surfaces.[6] The equation can be described as

$$h = \frac{\lambda}{2\pi n_0}\left[l\pi \pm \arcsin\sqrt{\frac{\Delta(1+\tilde{r})^2}{(1-\tilde{r})^2 + 4\tilde{r}\Delta}}\right] \quad (1)$$

In eq 1, $\tilde{r} = (n_0 - n_1)^2/(n_0 + n_1)^2$ is the Fresnel reflection coefficient for the air−solution interface, where n_0 is the refractive index of the film liquid (water in this paper), $n_1 = 1.499$ is the refractive index of the oil phase (squalene), $l = 0, 1, 2, 3...$ is the order of the interference, $\Delta = (I - I_{min})/(I_{max} - I_{min})$, I is the instantaneous intensity of the photocurrent, and I_{min} and I_{max} are its minimal and maximal values. The true film thickness can be smaller than the thickness determined by eq 1, which is referred to as the equivalent film thickness. The difference is due to the surfactant adsorption layers at the film surfaces. However, for the range of film thickness studied in the absence of surfactant in this paper, the difference was not significant and no correction to eq 1 has been made.

It is noted that the Scheludko cell was purposely left open within the clean room atmosphere (in contact with air). Therefore, the initial migration of dissolved gases from water into oil was expected but the reverse migration was also possible, depending on the contact time between the degassed oil and the water, as illustrated in Figure 1. Indeed, these two possible gas migration processes have different effects on the film drainage and stability as experimentally observed. It should be noted that the experimental system (the oil, the DI water, and the film formed) was for single use only.

3. Results and Discussion

Once the degassed oil and the nondegassed DI water were brought into contact, the dissolved gases in the water began to migrate from the water into the oil. Therefore, the water films formed at different contact times (measured from the moment of contacting the oil and the water in the Scheludko cell) should correspond to the different levels of degassing the film water. For reference, the oil-in-water emulsion systems formed using the nondegassed squalene were also investigated immediately after the oil and water were brought into contact and these systems are referred to as the zero contact time cases in this paper.

Two important parameters of the films were measured: the film lifetime as measured between the first and last interferograms, and the film thickness at rupture, called the critical thickness. Frequently, the dimples were formed and observed interferometrically but the long-lasting films normally drained until reaching plane-parallel film surfaces and then ruptured instantly.

The dependence of the film lifetime on the oil−water contact time is shown in Figure 2. The point at zero contact time shown in Figure 2 refers to the experimental data obtained with the nondegassed squalene and the DI water at instant contact. It was difficult to perform the film drainage measurements at zero contact time between the degassed oil and the DI water because at least 30 s was needed to set up the system for viewing and recording. This minimum time is given by the horizontal error bars in Figure 2. The vertical error bars describe the maximum relative errors of 10%, except the point at 10 min contact time, where the maximum relative error is 20%. The significant relative errors are due to the fact that the film rupture was strongly biased to (external) disturbances (which were minimized by the vibration isolation): the longer the film lifetime, the more considerable the effect of disturbances on the film rupture. It can be observed
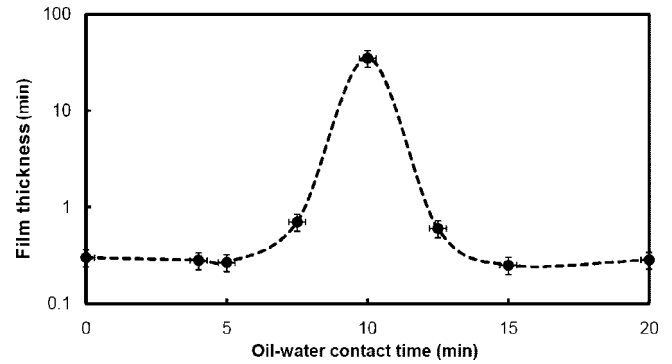
Figure 2. Film lifetime versus contact time between the DI water (film) and the oil (nondegassed at zero contact time, otherwise degassed). The line is used for eye guidance only.
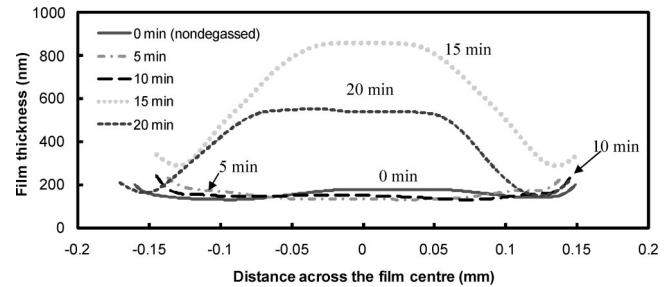
Figure 3. Film profiles measured from the interferograms taken before the film rupture as a function of the oil−water contact time.
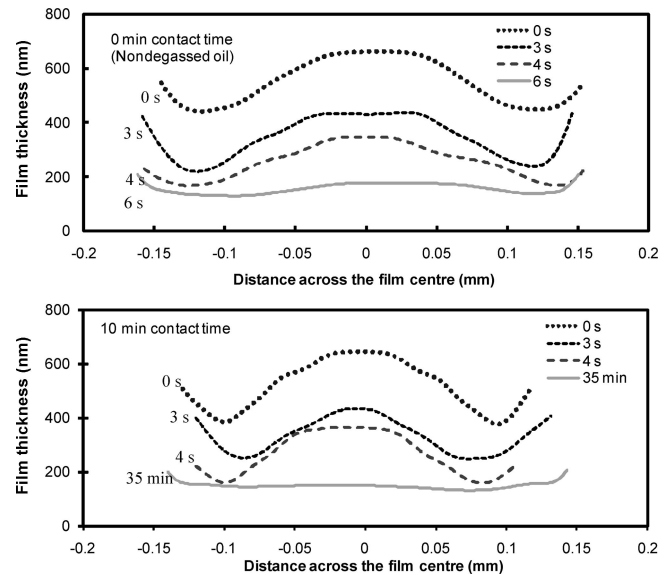
Figure 4. Evolution of film profiles measured at different drainage times, as shown by the legends attached to the curves, for the oil−water contact time of 0 (upper diagram) and 10 (lower diagram) min, respectively.

from Figure 2 that the contact time of about 10 min gave the longest film lifetime which was about 35 min. For shorter or longer contact time between the oil and the water, the film lifetime was short. It is hypothesized that the migration of dissolved gases between the DI water and the oil is the principal cause of the difference in the film lifetime observed. This hypothesis is supported by the film critical thickness at rupture and the evolution film profiles which are shown in Figures 3 and 4, respectively.

As shown in Figure 3, when the oil and the water were contacted for short time, i.e., shorter than 10 min, the critical film thickness (taken as the constant thickness before the film rupture)

Table 1. Constant Film Thickness before Rupture and Interfacial Potential As a Function of the Contact Time between the Degassed Oil and the DI Water

oil−water contact time (min)	a	5	10	15
constant thickness (nm)	153.64	144.88	145.02	NA
interfacial potential (mV)	−67.13	−63.69	−63.75	NA

[a] Nondegassed oil at instant contact time with the DI water. NA = not applicable.

was almost constant (about 150 nm). However, when the oil and the water were contacted for a long period of time, the films instantly ruptured at significantly thick thicknesses (i.e., at 840 and 540 nm for the oil−water contact time of 15 and 20 min, respectively). These values for the film thickness are larger than the range of DLVO (the electrical double layer and van der Waals interactions) forces. The probable driving force for the film rupture at the high thicknesses is the migration of dissolved gases ("adsorbed" from the ambient air by the oil) from the oil into the water film. The gas migration is caused by the difference in concentrations of dissolved gases in the oil and in the water. At short oil−water contact time, the gas migration is expected only from the water into the oil which can have an effect on decreasing the film drainage rate. At an optimal contact time (which was about 10 min in our experimental studies), the gas migration along the two directions can have a maximal stabilizing effect on the film drainage and stability.

The uncertainty of determining the initial film thickness and profiles as shown in Figure 4 is usually high because the initial film drainage was normally very fast and the on-set zero time was defined as the moment of the appearance of the first interferometric image which was measured within the (1 frame per second) recording frequency of the CCD camera used. The difference between the two initial film thicknesses could be as much as 100 nm. Importantly, dimples were observed at the initial drainage stages (Figure 4). The film profiles at short oil−water contact time were similar to those present for the zero contact time in Figure 4. However, the film profiles obtained at 10 min oil−water contact time were different and very flat at later stages. Both groups of films made at short (<10 min) and long (>15 min) oil−water contact times ruptured at the dimple periphery. Significantly, films made at the long contact times normally ruptured with dimples and at high thicknesses (>400 nm), probably due to the flux of dissolved gases from the oil phase into water films. For these dimpled films (made at long contact times), the film thickness before rupture also changed with time significantly and therefore the quasi-equilibrium analysis could not be applied.

For the short contact time cases, the films before rupture were almost stationary. The film thickness was nearly constant and the quasi-equilibrium analysis could be applied as follows. The balance between the capillary pressure and the pressure of the electrical double layer (EDL) interaction can be used to determine and check the variation of the interfacial potential. The van der Waals interaction can be ignored at the film thickness of 150 nm. The results are described in Table 1. For the high thickness, the EDL pressure can be calculated using the superposition approximation.[6] The pressure balance for 1:1 electrolytes gives

$$\frac{2\sigma}{R_c} = 64cRT \exp(-\kappa h) \tanh^2 \frac{\psi F}{4RT} \tag{2}$$

where R_c is the radius of the film holder (2 mm), σ is the oil−water interfacial tension, which is about 32 mN/m,[37] c is the electrolyte concentration, R is the gas constant, T is the absolute temperature, Ψ is the oil−water interfacial potential,

κ is the Debye constant, F is the Faraday constant, and h is the film thickness. For the DI water, pH = 5.8 corresponds to 2.5×10^{-6} M ionic strength. The interfacial potential shown in Table 1 is almost constant and agrees with the literature data for a similar oil−water interface.[38] Clearly, the degassing effect did not change the interfacial potential and the electrical double-layer repulsion between the oil−water interfaces.

3.1. General Discussion and Implication. The new experimental results obtained in this paper clearly show that migration of dissolved gases has a strong effect on the film rupture. The observation of the film rupture at very high thicknesses cannot be satisfactorily explained by the colloidal forces, in particular, the so-called hydrophobic force due to the restructuring of water molecules at hydrophobic surfaces which can extend over only a few water molecules. Importantly, the gas migration can be magnified in foam films and wetting films which are adjacent to the gas phase (the gas bubbles). For foam and wetting films, the gas migration from the bubble into the water film is predominant. (The reverse migration cannot be expected due to the gas concentration difference.) This situation is equivalent to the case of long oil−water contact time in this study and the effect of the gas migration on the film rupture can be most critical. If surfactants are used to stabilize the films, the gas migration can be reduced by the adsorbed layer of surfactants at the film surfaces and hence the effect of the gas migration on the surfactant-stabilized films can be decreased. In fact, the effect of gas migration on film stability can be significant even at high surfactant concentration[39−41] but has been largely neglected in predicting and analyzing the film instability.

It is hypothesized in the previous paragraph that after about 10 min of contact between the degassed oil and the (nondegassed) DI water film, the air migrates back to the water film and results in the film rupture. The hypothesized process of the hydrophobic air migrating back to the (hydrophilic) water instead of staying in the hydrophobic oil would be further explained. Since the degassed oil was purposely gassed by air on one side and by dissolved air in water on the film side (see Figure 1), at some stage the oil became fully gas-saturated while the film became degassed, with the concentration of dissolved gases being lower than the normal level (of 20 mL/L). The question as to why (hydrophilic) water under normal conditions contains 20 mL/L of dissolved (hydrophobic) gases from air is out of the scope of this paper but the available literature can be found; e.g., see refs 42−44. The lowered concentration of dissolved gases in water film is the driving force for the air migration from the oil phase to the water. It is also noted that the (near) complete degassing of oil is significant to the experiments and a few hours were normally required to vacuum the dissolved gases in oil. It is also interesting that the film thickness, as determined before rupture, at 15 min of contact (~800 nm) is more than the thickness at 20 min (~600 nm), indicating that the systems are indeed very dynamic. The dynamic nature of the systems at long contact times between the oil phase and the water film is amplified by the migration of

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dissolved gases around the dimple periphery and by the possible coalescence of the sub-micrometer bubbles (and with the macroscopic bubble).

Emulsions have numerous applications in various fields such as food, chemical, pharmaceutical, cosmetic, paint, and oil industries.[1] There are basically two basic types of emulsions: oil-in-water (OW) emulsions and water-in-oil emulsions. The OW emulsions can be considered as hydrophobic (very unstable) colloidal dispersions and surfactants are usually used to stabilize the systems. It is commonly assumed that the long-range hydrophobic force is responsible for the instability.[45] However, it was established recently that surfactant-free OW emulsions and hydrophobic suspensions can be stabilized by degassing.[46−48] These macroscopic studies significantly support the micro- and nanometer scaled results obtained and reported in this paper. Importantly, we show that migration of dissolved gases in and out of the water films has different effects on the film drainage and stability. Hopefully, the new results will stimulate the new theoretical analysis of film drainage and rupture. For instance, equations for film drainage and rupture[49,50] will have to be modified to include migration of dissolved gases which are present in water as clusters of nanometer-sized bubbles.[51,52]

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4. Conclusion

A new innovative experimental method and procedure was developed to investigate the effect of dissolved gases on liquid film drainage and stability. The method involves contacting degassed oil and nondegassed water at different times and examining the oil-in-water films using microinterferometry with the Scheludko cell and thin film balance. The results have shown that gases inherently dissolved in water have a significant effect on the film rupture. In particular, films of deionized water in contact with degassed oil (squalene) were stable for as long as 35 min, while the water films in contact with nondegassed oil could not last longer than a fraction of minutes. All these films ruptured at a constant film thickness of about 150 nm. On the contrary, the oil-in-water emulsion films formed between the degassed oil left in contact with air for a long period of time (15−20 min) did not last longer than a few seconds but ruptured at significantly high thicknesses (of the order of 800 nm). The degassing did not change the interfacial potential (about −65 mV) and the electrical double-layer repulsion between the oil−water interfaces. The results were justified in terms of migration of dissolved gases between oil and water. The gas migration out of and into the film caused the different rupture phenomena observed.

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