

NOTE

Investigation of Thin Aqueous Films on Silica Using a Modified Interferometric Technique

The thinning behavior of liquid films between free bubbles and silica is investigated using the interferometric technique. Stable films were obtained at higher salt concentrations compared to previous studies because of the improved cleaning procedure. In contrast to the captive bubble technique used in the past, the free bubble method employed more closely approximates such processes as flotation. The results obtained for aqueous films at low and high ionic strengths are in better agreement with theoretical predictions than those in previous studies.

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Key Words: micro-interferometric technique; free bubble method; disjoining pressure; thin aqueous films; silica.

INTRODUCTION

Thin liquid films that form between liquids, gases, and solids are of significant importance in many industrial and biological systems (1–5). Rupture of these liquid films (6–10) on solid surfaces is a critical step which governs the efficiency of processes such as detergency and flotation. Here, we have used a modified interferometric technique and an improved cleaning procedure to accurately measure the thickness of the thin liquid film between a free gas bubble and a mineral plate.

MATERIALS

The solid substrate used was a fused vitreous silica disk (supplied by the Oriol Corporation), 12.7-mm diameter and 6-mm thick, polished flat to within 0.05 wavelength of visible light.

The gas was oil free nitrogen supplied by the T. W. Smith Corporation, which was passed through ascarite (Arthur H. Thomas Company) to remove CO₂, passed through distilled water, and then filtered (0.22- μ m pore size, 25-mm diameter Milipore MF filter in stainless steel holder) to remove dust. The KCl used was ACS reagent grade supplied by Fisher Scientific, which was roasted at 663 K for 3 h prior to use.

The silica and the Teflon cell cover housing the silica plate were cleaned before every measurement using an elaborate stepwise procedure considered to be an improvement over a previously used method (11). The cell, including the silica plate, was soaked in chromic acid solution (9 lb of ACS grade sulfuric acid and 1 bottle of Manostat cromerge; chromic acid prepared by electronic grade sulfuric acid caused the Teflon cell cover to turn yellow) for 15 min. The chromic acid was washed away with distilled water. The same procedure was followed with alcoholic KOH (12.5 g of KOH, 84 ml of 200 proof ethanol, and 16 ml of distilled water) and with 0.1 M nitric acid (ACS electronic grade, Amend Co.). As suggested by Aronson and Princen (11), all cleaning solutions were discarded after one use.

The cleaning procedure was checked in the following manner: the cell was filled with either triply distilled water or salt solution and several film thicknesses

were measured. If it did not correspond to the previously measured thickness (evidence of surface nonreproducibility), or if any sign of film instability was observed, the cleaning procedure was repeated.

METHODS

Film thickness can be estimated by monitoring capacitance (12) or conductance, or using various techniques such as ellipsometry (6) or interferometry (13). Interferometry is used in this study because it is the most suitable method for studying the nonequilibrium behavior of films.

Past interferometric work (11, 13–16) on the thinning and rupture of aqueous surfactant films has been carried out using the captive bubble method. In this method, the gas bubble is gently pressed against the solid substrate, which is submerged in the solution (Fig. 1a). Since the bubble is motionless, kinetic processes such as film thinning and rupture are easily followed.

In the free bubble method used in this study, the gas bubble is allowed to rise due to buoyancy until it contacts the solid (9) (Fig. 1b). Therefore, this method approximates flotation and other thin film processes much more realistically than do captive bubble experiments. However, this method has not been used extensively in the past because of such problems as in controlling the motion of the bubble and the effect of mechanical vibrations.

APPARATUS

Figure 2 shows a cross-sectional view of the apparatus. Nitrogen gas is released through a capillary tube (0.06-cm o.d.) at a pressure controlled by a 0.25-cc gas syringe (Fisher Scientific). The capillary holder is equipped with a vertical positioner so that the distance between the capillary tip and the plate bottom, and hence the velocity of contact, can be altered. A cathetometer is used to measure the bubble size. The silica disk is housed in the Teflon cover of the cell, which is also made of silica. The Teflon cover rests on the cell only by gravity, to prevent contamination from sealants. The cover also contains openings for the capillary tube and for a suction tube to remove the solution after the measurement.

The system is viewed from above under monochromatic illumination (100-W HBO Hg Lamp from Zeiss Corp. fitted with a 546.1-nm Å Zeiss Corp. or a 435.0-nm Å Oriol Corp. filter), using a Zeiss Universal microscope. Light reflected by the film may be directed either to the eyepiece or, through a phototube for photographic recording, and the light intensity is read from a photometer. The optical arrangement is the same as that used by Aronson and Princen (11). Various modifications were made to the Zeiss AC stand to damp out random vibrations (17).

MEASUREMENTS

(a) Thickness

In the micro-interferometric method, the relation between the light intensity reflected from the film and the film thickness is expressed by Eq. [1], assuming

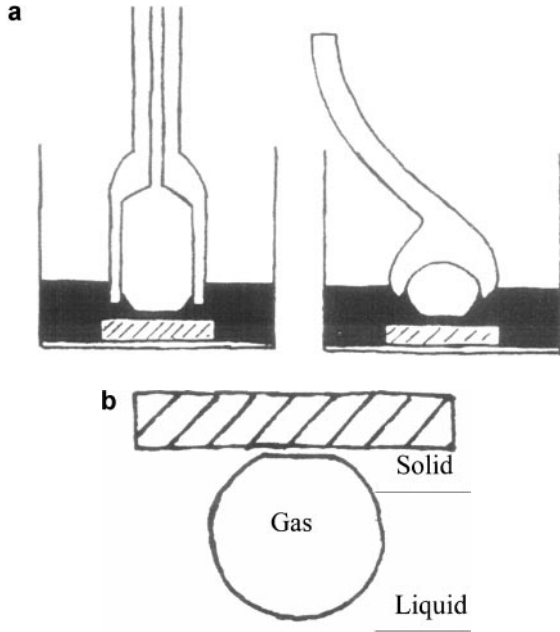


FIG. 1. (a) Captive bubble method. Gas bubble pressed against solid. (b) Free bubble method. Gas bubble contacts the solid due to buoyancy.

that the incident beam is perpendicular to the film and that light absorption is negligible within the film:

$$\frac{I}{I_0} = \frac{r_2^2 + r_3^2 + 2r_2r_3 \cos J}{1 + r_2^2r_3^2 + 2r_2r_3 \cos J}, \quad [1]$$

where I is the intensity of the reflected light and I_0 is the intensity of the incident light.

$$r_1 = \frac{n_1 - n_3}{n_1 + n_3}, \quad r_2 = \frac{n_2 - n_1}{n_2 + n_1}, \quad r_3 = \frac{n_3 - n_2}{n_3 + n_2}, \quad \text{and} \quad J = \frac{4\pi n_2 h}{\lambda}. \quad [2]$$

r_1 , r_2 , and r_3 are the reflectivities of the silica-air, silica-solution, and the solution-air interfaces, respectively, n denotes the refractive index (values taken from Ref. 19), the subscripts 1, 2, and 3 denote the media (silica, solution, and air, respectively), λ is the wavelength of the light used, and h is the film thickness to be determined.

Previous investigators (14, 20) used a ratio Δ to account for background illumination:

$$\Delta = \frac{I_f - I_m}{I_M - I_m}, \quad [3]$$

where I_f is the recorded intensity for the film and I_m and I_M are the minimum

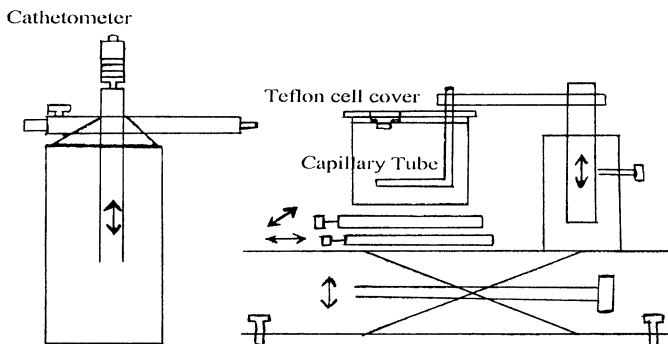


FIG. 2. The cell system showing the vertical positioners and cathetometer.

and maximum recorded intensities of the reflected light. The advantage of Δ is that random reflection of light from outside sources and from the sides of the gas bubble may be neglected. The equation for film thickness may be derived from substitution of Eq. [3] into Eq. [1] (14, 20).

The method just described is suitable only for captive bubbles. Difficulties arise with the higher sensitivity of the free bubbles to vibration due to their increased mobility. Direct measurement of the maximum and minimum intensities with a photometer is not easily achieved due to the small size of Newton's Rings (17). Therefore, a new method better suited for free-bubble experiments for the measurement of film thickness was developed.

This method replaces the maximum and minimum reflected intensities by those of a ruptured film and an infinitely thick film, denoted by I_{rupt} and I_∞ , respectively. I_{rupt} is modeled as the intensity of light reflected back from the silica/air interface. I_∞ is modeled as the intensity of light reflected back from the silica/solution interface. In a similar fashion, a ratio Δ_∞ is introduced, so that random reflections from outside sources and the sides of the gas bubble can be neglected.

$$\Delta_\infty = \frac{I_f - I_\infty}{I_{rupt} - I_\infty} \quad [4]$$

As before, substituting Eq. [4] into Eq. [1] and rearranging

$$\cos J = \frac{\left[(1 - \Delta_\infty) \left(\frac{r_2^2}{1 - r_2^2 r_1^2} \right) + \Delta_\infty \left(\frac{r_2^2}{1 - r_2^2 r_3^2} \right) \right] (1 + r_2^2 r_3^2 - r_1^2 r_2^2 - r_1^2 r_3^2) - r_2^2 - r_3^2}{\left[(1 - \Delta_\infty) \left(\frac{r_2^2}{1 - r_2^2 r_1^2} \right) + \Delta_\infty \left(\frac{r_2^2}{1 - r_2^2 r_3^2} \right) \right] (2r_1^2 r_2 r_3 - 2r_2 r_3) + 2r_2 r_3}. \quad [5]$$

From [5] and [2], the film thickness h can be calculated, where r_4 is the reflectivity of the silica-air interface and is numerically equal to $(-r_1)$.

(b) Disjoining Pressure

The disjoining pressure exerted by a stable equilibrium film resists the forces leading to its thinning. It is denoted by Π and defined as $\Pi = P_f - P_l$, the difference between the film pressure, P_f , and the bulk liquid pressure, P_l .

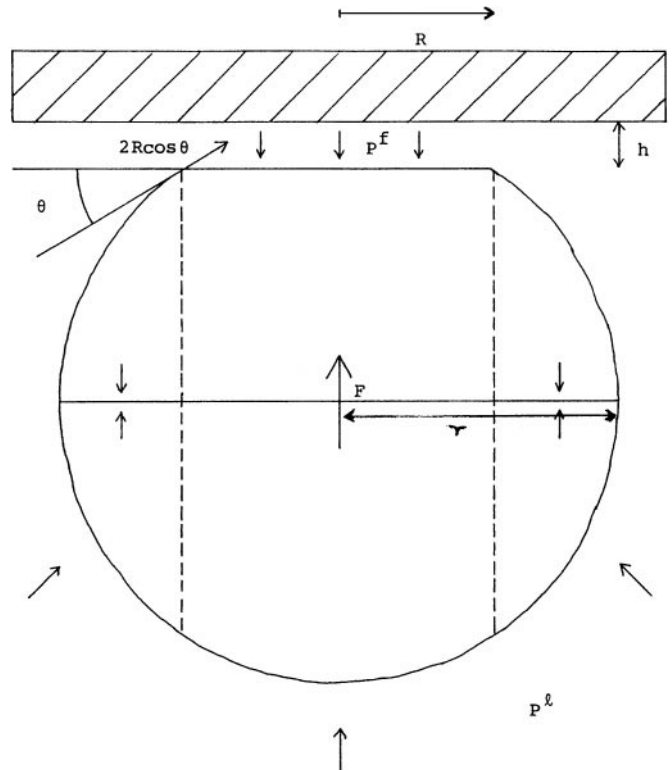


FIG. 3. Force balance on a wetting film.

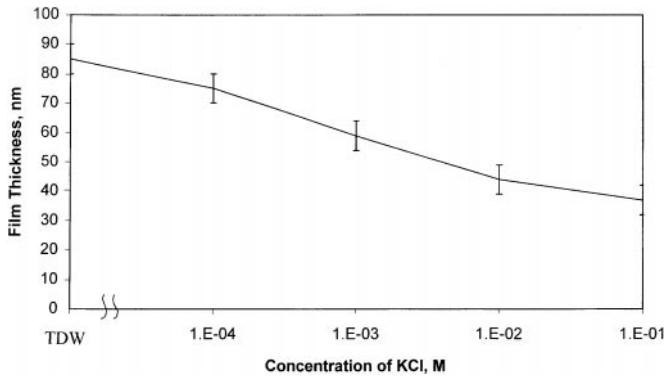


FIG. 4. Effect of salt on film thickness at a capillary pressure of 2×10^{-7} mN/m².

Performing a force balance on the system, as shown in Fig. 3,

$$V \Delta \rho g + P_1 \pi R^2 - P_f \pi R^2 + 2\pi R \gamma \sin \theta = 0. \quad [5]$$

where $V \Delta \rho g$ is the buoyancy of the bubble, $P_1 \pi R^2$ is the force exerted by the bulk on the bottom cylindrical section of the sphere, $P_f \pi R^2$ is the force exerted by the film acting against the bulk, and $2\pi R \gamma \sin \theta$ is the force due to the surface

tension of the bubble–liquid interface. Rearranging and assuming the bubble to be a perfect sphere ($R \ll r$) and $\theta \sim 0$,

$$\Pi = \frac{4gr^3 \Delta \rho}{3R^2}. \quad [6]$$

The capillary pressure P_c is defined as

$$P_c = P_g - P_l,$$

where P_g is the gas pressure.

For a free bubble,

$$P_c = \frac{2\gamma}{r},$$

where γ is the surface tension of the air–solution interface.

At equilibrium, the film pressure and the gas pressure must be equal, i.e., $P_f = P_g$, and hence, $\Pi = P_c$.

Therefore,

$$\Pi = \frac{2\gamma}{r}. \quad [7]$$

Combining Eqs. [7] and [6] with known values of ρ and γ for pure water at 295 K (assuming $\Delta \rho \sim \rho$), $r^4 = 0.11053R^2$ in CGS units.

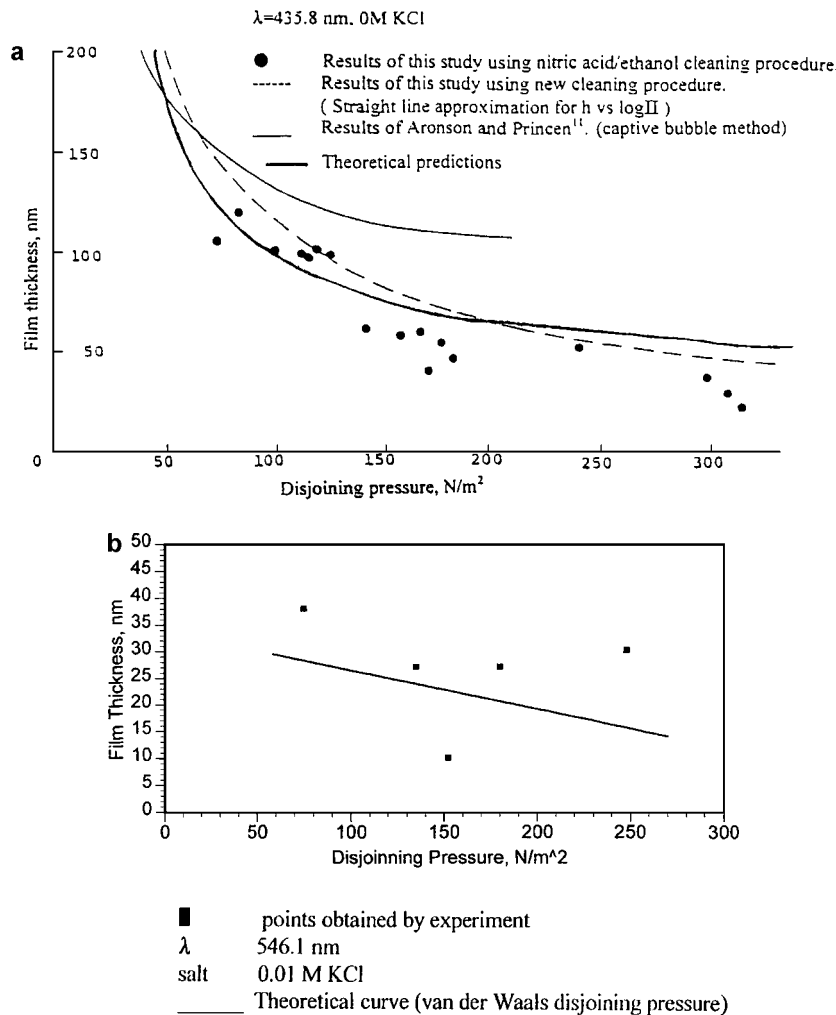


FIG. 5. (a) Comparison of Π – h isotherms obtained using the free-bubble and captive-bubble methods. (b) Comparison of theoretical predictions with experimental data for films of high ionic strength.

Hence,

$$\Pi = \frac{2\gamma}{(0.11053R^2)^{1/4}} \approx \frac{144.6}{(0.11053R^2)^{1/4}} \quad [8]$$

Thus, by measuring the film radius, the disjoining pressure can be estimated.

RESULTS AND DISCUSSION

The effect of ionic strength on the thickness of thin films is shown in Fig. 4 for a disjoining pressure of 2000 dyn cm². At high ionic strengths, electrical double-layer interactions will be suppressed, permitting reduction of the film thickness. Read and Kitchener (21) were unable to get equilibrium films at electrolyte concentrations greater than 10⁻³ M due to hydrophobic contamination and dust particles. Equilibrium films of concentrations up to 0.1 M KCl could be obtained in the present case due to the sophisticated cleaning procedure used.

The film thickness–disjoining pressure isotherms obtained experimentally using the free-bubble and captive-bubble techniques are compared in Fig. 5a, with those obtained using theoretical predictions for pure water. Read and Kitchener (21) calculated the theoretical values from the tables of Devereux and de Bruyn (22), using the ζ -potentials determined for silica by Jones and Wood (23). These calculations are based on the Guoy–Chapman diffuse double-layer theory.

It can be seen that the free-bubble method used in the present investigation is in better agreement with the theory than the captive-bubble method (11, 20). To show that the cleaning procedure does not account for this difference, data obtained using the cleaning procedure used by previous investigators (11, 21) is also plotted. These results show that the use of the previous cleaning method reduces the measured thickness, thus increasing the difference between the results given by the two methods. This is expected because the ζ -potential of hydrophobic silica is equivalent to that of clean, hydrophilic silica, and thus the thickness should be the same. The slight decrease in thickness is due to the many hydrophobic spots, which tend to reduce the overall film thickness. The error in the captive bubble technique could be due to the effect of containing the bubble in a holder and/or the incorrectness of the equation used to compute the disjoining pressure.

The Π - h isotherm for 10⁻² M KCl solution is plotted in Fig. 5b. The theoretical curve is the van der Waals disjoining pressure calculated using values based on optical dispersion data reported by Gregor (24) and reproduced by Read and Kitchener (21). The good agreement between the measured values and the theory confirms the prediction of van der Waals repulsion between silica–water and water–air interfaces. This is attributed to the fact that, for stable films at high electrolyte concentrations, electrostatic effects are almost completely suppressed.

CONCLUSIONS

In this study, stable films at concentrations of electrolyte higher than those previously reported could be obtained because of an improved cleaning procedure. As predicted by the electrical double-layer theory, film thickness decreased as the ionic strength increased. The results obtained for films formed at high ionic strength confirm the prediction of positive disjoining pressure between the silica–water and air–water interfaces.

The free-bubble method gave results that are in better agreement with the theoretical predictions than the captive-bubble method. The free-bubble method, while less convenient, has no unknown effects that exist when the gas is contained in a holder and, in addition, has a clearly defined and easily calculable disjoining pressure. Moreover, the free-bubble technique is a more realistic approximation of processes like froth flotation. This technique is useful for elucidating the mechanisms involved in the attachment of bubbles to particles in processes such as flotation.

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P. Somasundaran*¹
S. Simpson†
R. K. Jain‡
I. Ivanov§
V. Raghuraman*

*NSF IUCR Center for Advanced Studies

in Novel Surfactants

Langmuir Center for Colloids and Interfaces

Columbia University 911 Mudd Building

New York, New York 10027

†Rogers Corp.

One Technology Drive

Rogers, Connecticut 06263-0188

‡Steele Laboratory for Tumor Biology

Massachusetts General Hospital

Boston, Massachusetts 02114

§University of Sofia

Faculty of Chemistry

Lab. of Thermodynamics, Physico-Chemical

Hydrodynamics

1126 Sofia, Bulgaria

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¹ To whom correspondence should be addressed.