

Thinning and Rupture of Aqueous Surfactant Films on Silica

P. Somasundaran,^{*,†} S. Simpson,[‡] I. Ivanov,[§] R. K. Jain,^{||} and D. Sarkar[†]

NSF IUCR Center for Advanced Surfactants, Langmuir Center for Colloids and Interfaces, 911 Mudd Building, Columbia University, New York, 10027, Rogers Corp., One Technology Drive, Rogers, Connecticut 06263-0188, Laboratory of Thermodynamics, Physico-Chemical Hydrodynamics, Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria, and Steele Laboratory for Tumor Biology, Massachusetts General Hospital, Boston, Massachusetts 02114

Received October 16, 1998. In Final Form: July 9, 1999

The thinning and rupture of aqueous surfactant films on silica is investigated using the interferometric technique and free bubbles, which approximate flotation more realistically than the captive bubble method. Different rupture mechanisms are observed at different pH values for aqueous films of dodecylamine on silica, explaining the pH dependence of quartz flotation using amine. While at low pH rupture is accompanied by the breaking off of a large drop in the center and subsequent formation of large irregular drops, at high pH ruptured spots grow to large circular drops.

Introduction

Rupture of thin liquid films between liquids, gases, and solids plays a governing role in determining the stability of bubbles and droplets in foams, emulsions, froths, and even biological cells.^{1–5} Behavior of liquid films on solids is particularly relevant to many processes such as detergency and froth flotation of minerals. While much work has been done on the rupture of liquid films^{6–8} and aqueous films on solids,^{9,10} very little has been done on the films of surfactant solutions on solid minerals, even though the rupture of these films is the critical step that determines the efficiency of processes such as flotation. In this paper, we have investigated the rupture mechanisms of aqueous films of dodecylamine on quartz.

Materials

The silica substrate, nitrogen gas, and potassium chloride are the same as described elsewhere.¹² The surfactant used was dodecylamine hydrochloride ($\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\cdot\text{HCl}$) from Eastman Kodak Co. The pH of the surfactant solutions was adjusted

using ACS reagent grade KOH, supplied by Amend Drug and Chemical Co., and 0.1 N HCl, supplied by Fisher Scientific. The pH of all the surfactant solutions was checked before and after the experiment.

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 efficacy of our cleaning procedure is demonstrated¹² by stable films obtained at salt concentrations higher than those obtained previously.¹¹

Methods

In the free bubble method used in this study, the gas bubble is allowed to rise due to buoyancy until it contacts the solid.^{9,12} Therefore, this method approximates flotation and other thin film processes much more realistically than do captive bubble experiments, in which the gas bubble is gently pressed against the solid substrate.^{11,13–16} The bubble is generated by pushing purified nitrogen with the help of a syringe through a capillary lying below the surface of the silica test slide. The behavior of the bubble was monitored with the help of a microscope lying above the slide. The slide along with the cell was washed repeatedly with chromic acid and alcoholic potash to ensure the complete removal of any organic contaminants. The apparatus along with the experimental procedure is described in detail elsewhere.^{12,17}

Results and Discussion

The study of the effect of amine on the characteristics of thin aqueous films is important because of its widespread use as a collector for quartz flotation. Flotation of quartz using dodecylamine depends on such variables as amine concentration and solution pH, which govern surfactant adsorption and surface tension.²⁵ Flotation

* Corresponding author.

† Columbia University.

‡ Rogers Corp.

§ University of Sofia.

|| Massachusetts General Hospital.

(1) Kirkpatrick, R. D.; Lockett, M. J. *Chem. Eng. Sci.* **1974**, *29*, 2363.

(2) Allan, R. S.; Charles, G. E.; Mason, S. G. *J. Colloid Sci.* **1961**, *16*,

150.

(3) Charles, G. E.; Mason, S. G. *J. Colloid Sci.* **1960**, *15*, 236.

(4) MacKay, G. D. M.; Mason, S. G. *Can. J. Chem. Eng.* **1963**, *Oct*,

203.

(5) Hodgson, T. D.; Lee, J. C. *J. Colloid Interface Sci.* **1969**, *30* (1), 94; *30* (4), 429.

(6) Derjaguin, B. V.; Zorin, Z. M. *Proc. Int. Congr. Surf. Act.*, **2nd** **1957**, 145.

(7) Mysels, K. J.; Shinoda, K.; Frankel, S. *Soap Films*; Pergamon Press: London, 1959.

(8) Princen, H. M.; Overbeek, J. T. G.; Mason, S. G. *J. Colloid Sci.* **1967**, *24*, 125.

(9) Derjaguin, B. V.; Kussakov, M. M. *Acta Physicochim. URSS* **1939**, *10* (1), 25; *10* (2), 153.

(10) Derjaguin, B. V.; Landau, L. *Zh. Eksper. Teor. Fiz.* **1941**, *11*,

802.

(11) Aronson, M. P.; Princen, H. M. *Colloid Polym. Sci.* **1978**, *256*,

140.

(12) Somasundaran, P.; Simpson, S.; Jain, R. K.; Ivanov, I.; Raghuraman, V. *J. Colloid Interface Sci.*, submitted for publication.

(13) Shelukdo, A.; Ekserova, D. *Dokl. Akad. Nauk. SSSR* **1959**, *127*,

149.

(14) Blake, T. D. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 192.

(15) Manev, E. MS Thesis, University of Sofia, Fac. Chimie, 1961.

(16) Manev, E.; Pugh, R. J., SME Annual Meeting, Feb 1992.

(17) Simpson, S. M.S. Thesis, Department of Chem. Eng., Columbia University, New York, NY, 1979.

(18) Vasicek, A. *Optics of Thin Films*; North-Holland Pub. Co.: Amsterdam, 1960 (English Ed., Interscience Pub., New York, 1960).

(19) Landolt, H. *Physikalisch-chemisch Tabellen*; Springer: Berlin, 1883.

(20) Blake, T. D.; Kitchner, J. A. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1435.

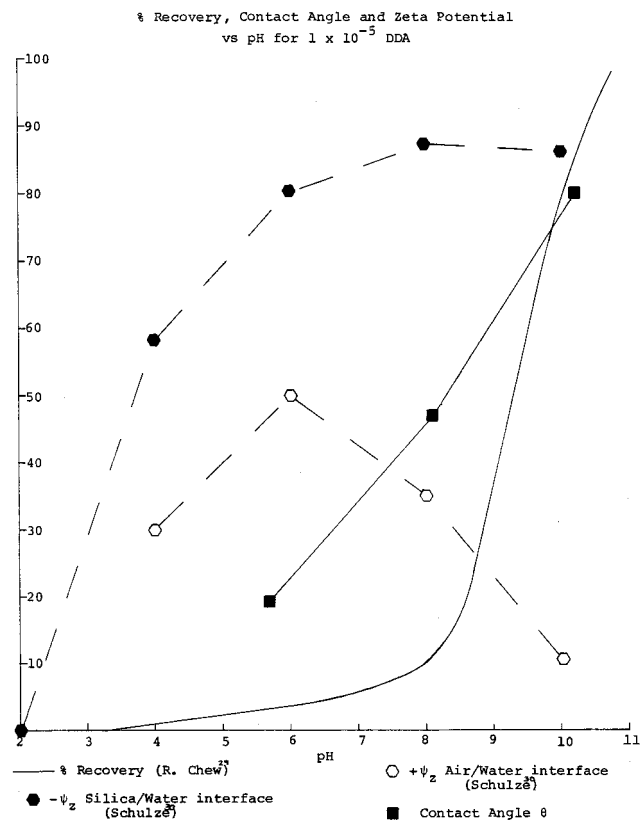


Figure 1. Quartz flotation compared with surface charges and contact angle as a function of pH (10^{-5} M DDA).

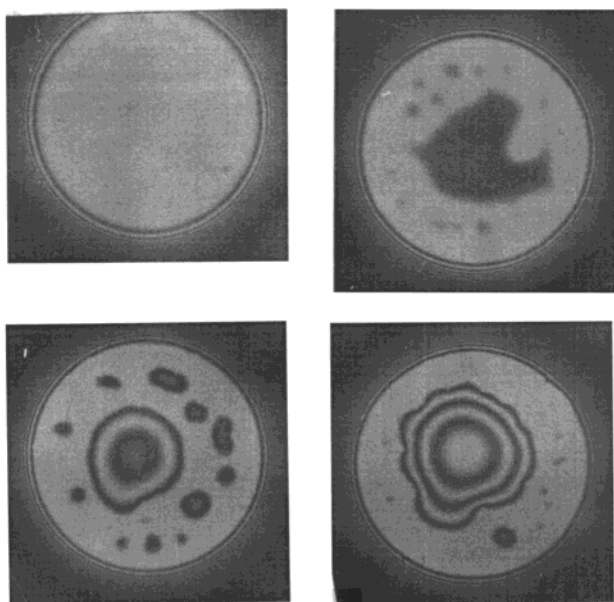


Figure 2. Film thinning and formation of droplets (1×10^{-8} M DDA, pH ~ 5.6).

begins at 5×10^{-5} M amine and is maximum at pH 10.5 for all amine concentrations. Around pH 10.2–10.5, the amine molecule and the ammonium ion exist in equal amounts.²⁶ It has been hypothesized²⁷ that they exist as ion–molecule dimers along with monomers in solution at

(21) Read, A. D.; Kitchener, J. A. *J. Colloid Interface Sci.* **1969**, *30* (3), 391.

(22) Devereux, O. F.; De Bruyn, P. L. *Interaction of Plane Parallel Double Layers*; MIT Press: Cambridge, MA, 1963.

(23) Jones, G.; Wood, L. A. *J. Chem. Phys.* **1948**, *13*, 106.

(24) Gregory, J. Ph.D. Thesis, University of London, 1964.

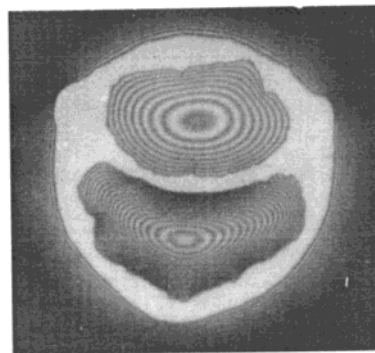


Figure 3. Irregular film (after 2 days) (1×10^{-8} M DDA, pH ~ 5.6).

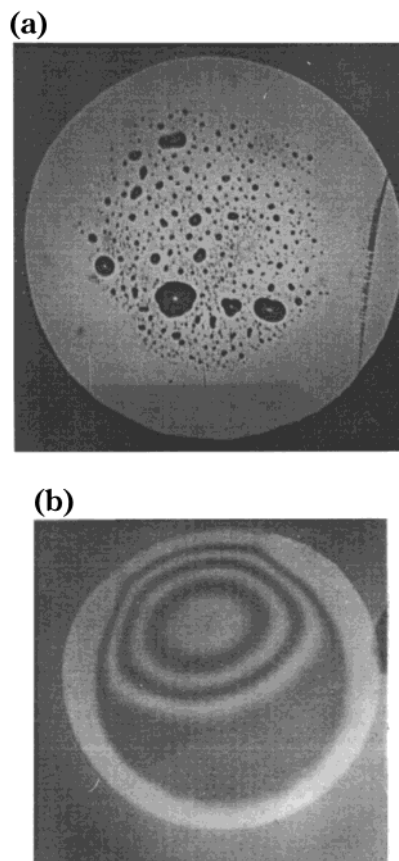


Figure 4. (a) Peripheral rupture. Note central drop breaking off (1×10^{-6} M DDA, pH ~ 5.6). (b) Formation and growth of large, irregular droplets (1×10^{-6} M DDA, pH ~ 5.6).

that pH. Flotation is maximum due to the high surface activity of the dimer complex. Complexation decreases repulsion between the ammonium ions because of shielding by the amine half of the dimer. The adsorption of amine on silica at a concentration of 10^{-5} M has been determined as a function of pH.²⁸ Below the point of zero charge (pzc) of silica (pH ~ 2), no adsorption occurred. Adsorption gradually increased until pH ~ 5 as the number of negative sites on silica increased. Adsorption remained constant until it rose to a maximum between pH 10 and 11.5 and then dropped to zero by pH 12. Results obtained for surface

(25) Bleier, A.; Goodard, E. D.; Kulkarni, R. D. *Structural Effects of Amine Collection Flotation, A. M. Gaudin Memorial Vol. 1*; Fuerstenau, M. C., Ed.; AIME: New York, 1976; p 117.

(26) Somasundaran, P. *Int. J. Miner. Process.* **1976**, *3*, 35.

(27) Ananthpadmanabhan, K.; Somasundaran, P.; Healy, T. W. *Trans. Soc. Min. Eng. AIME* **1978**, *266*, 2003.

(28) Petrov, I.; Panaitov, I.; Panaitov, D. *Fac. Chim.* **1974**, *69*(2), 37.

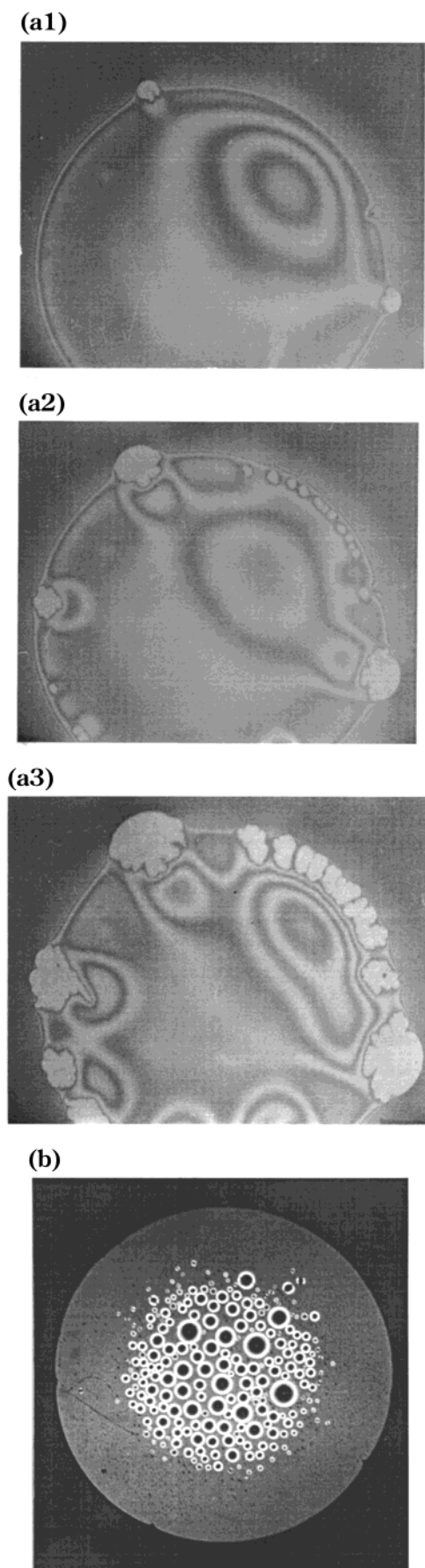


Figure 5. (a) Spot rupture (1×10^{-6} M DDA, pH ~ 10.5) at time (1) 0 s, (2) 5 s, (3) 20 s. (b) Formation and growth of circular droplets (1×10^{-6} M DDA, pH ~ 10.5).

tension²⁶ show that the 4×10^{-4} M amine solution exhibits a minimum at a pH of 10.2.²⁷

The attachment (flotation) of bubbles to particles can be attributed to two basic characteristics of the thin film: the film rupture and the advance of the contact angle. In Figure 1, the flotation of quartz particles (Chew²⁹) is compared with the surface charge (Schulze³⁰) and contact angle for ruptured films for 10^{-5} M DDA over a range of pH values. While electrostatic force is not the only force leading to the rupture, it by far has the predominant effect. It is clear from Figure 1 that, in the high pH range where flotation is increasing, the electrostatic impetus toward rupture does decrease, while the contact angle increases considerably. At low pH, however, it appears that the opposite is true. The contact angle rises only slowly, while the surface charge effect increases, although to a lesser extent because of a reduction in the silica surface charge with increasing surfactant adsorption. Flotation of quartz with DDA at low pH is attributed to electrostatic effects, although the contact angle must be large enough such that the bubble is not dislodged by agitation.

This apparent difference in the predominant force governing attachment at low and high pH leads one to suspect that the rupture characteristics of the thin films may be different at low and high pH. Therefore, the film rupture mechanisms of amine films on quartz at high and low pH were studied using the free-bubble method.

Before presenting the results, it will be useful to review the following observations made by Shelukdo^{31,32} for soap films but equally applicable to aqueous films on silica: (i) Thick films will always have a convexity in the center. This is known as a dimple. (ii) Upon thinning of the film, the convexity decreases, and at small thickness, the film appears to be plane-parallel. (iii) Upon further thinning of the film, either a stable film will form or the film will rupture when it reaches a critical thickness. After rupture, either the gas will spread on the surface or a very thin film will form. This film is white and corresponds to black films formed by soap films.⁷

At very low concentrations of DDA stable films are formed at all pH values. When 10^{-8} M DDA is reached, the film continuously thins, droplets appearing on its surface (Figure 2). After 2 days, the film appears as a ruptured film (Figure 3), actual rupture never having occurred.

As the concentration is increased, actual rupture occurs. At low/natural pH (~ 5.8), this manifests in what we term *peripheral rupture* (Figure 4a), in which an area on the periphery of the film ruptures and instantaneously begins to expand around the edge of the film. When the two ends meet (this has just occurred at the top in Figure 4a), a central drop is broken off. As the edge expands to reach the final contact angle, this large drop migrates to the center of the ruptured film followed by the formation and growth of large, irregular droplets (Figure 4b), in agreement with previous observations of Schulze³³ and Aronson and Princen.¹¹

The characteristics of rupture are different at high pH (~ 10.5) as shown in Figure 5a. This type of rupture, which we call *spot rupture*, begins with the formation of ruptured spots at the periphery which grow, meet each other breaking off a central drop, and finally expand as a single

(29) Chew, R. Personal communication, Columbia University.

(30) Schulze, H. J. *Colloid Polym. Sci.* **1975**, *252*, 730.

(31) Shelukdo, A. *Adv. Colloid Interface Sci.* **1967**, *1*, 391.

(32) Shelukdo, A. *Colloid Z.* **1957**, *155*, 39.

(33) Schulze, H. J. *Proc. Int. Conf. Colloid Surf. Sci. (Budapest)* **1975**, *1*, 179–186.

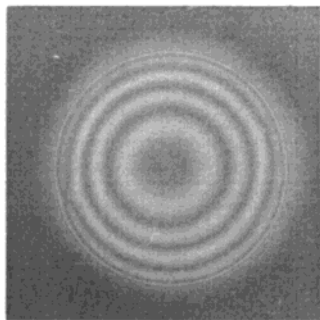


Figure 6. Dimple formation (elapsed time ~ 10 min) (1×10^{-2} M DDA, pH ~ 5.6).

edge to reach the final contact angle. As at low pH, droplets form and grow but are circular in shape (Figure 5b).

The differences in rupture characteristics can be explained on the basis of the previous observations on flotation. At low pH, the predominant force is electrostatic, and once a spot is ruptured, since its edges are closer to the silica surface, it expands rapidly as the two interfaces are strongly attracted. At high pH, however, this attraction is not as strong and the first hole formed does not expand over the whole film. Instead, many spots have time to form, their expansion and the final rupture being due to the contact angle advance.

If the concentration of the cationic surfactant is increased (above the cmc), stable films are once again formed (at natural pH). This is attributed to the formation of a bilayer adsorbed at the silica/solution interface. Figure 6 shows a stable film formed in 2×10^{-2} M DDA solution at pH 5.6 with spontaneous dimple formation. In earlier studies¹¹ with another cationic surfactant, stable films have been observed at concentrations above the cmc.

Summary

The rupture characteristics of thin dodecylamine films on silica are markedly different at low and high pH, when observed at concentrations below the cmc. At low pH, rupture occurs due to a large central drop breaking off followed by the formation of large irregular droplets. At high pH, on the other hand, many ruptured spots form, gradually growing into larger circular droplets. The marked pH dependence of quartz flotation using amine is accounted for by this difference in mechanism.

Acknowledgment. The authors acknowledge the financial support of the NSF Industry/University Cooperative Research Center (IUCRC) for Advanced Studies in Novel Surfactants at Columbia University, the National Science Foundation Grant Nos. EEC-9804618 and CTS-9622781, and the Industrial Partners of the IUCRC.

LA9814485