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STABILITY OF AQUEOUS FILMS BETWEEN BUBBLES:

Part 2: Effects of trace impurities and evaporation

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Abstract

The stability of water films has been investigated with a Mysels-Scheludko type film balance. Minor trace impurities in water do not affect the lifetime of water films under vapor saturation, but significantly influence the stability in free evaporation. Trace amounts of positively adsorbed contaminants induce Marangoni-driven flow that destabilizes films under evaporation conditions whereas negatively-adsorbed electrolytes actually prolong stability by reversing interfacial tension gradients and driving a steady circulation within the film. At high thinning rates, pure-water films develop exotic-appearing flow patterns and break due to a strong coupling between hydrodynamic and interfacial tension-gradient adsorption stresses. The most dominant factor of transient film stabilization in dynamic conditions under evaporation is a surface tension gradient created in the film. We discuss surface tension gradients in transient films created by temperature differences, impurity concentration, and expansion of the films.

Keywords

water films; bubble coalescence; disjoining pressure; surface tension gradient; Marangoni effect

1. INTRODUCTION

The stability of water films, or the lifetime of air bubbles in water, is affected by various conditions. In a previous paper¹ (Part 1), we have shown that electrical double layer forces between air-water interfaces stabilise a uniform water film when the two air-water interfaces approach at less than 1 $\mu\text{m/s}$. Films formed with highly purified water were stable but the purity of water, and consequently the stability of the film, changes as soon as the film is exposed to an environment, including air. Here, we report on films formed from water prepared in various ways, and discuss the stability of water films affected by trace amounts of surface active impurities.

We also observed in Part 1 that transient water films are formed when the thinning speed is between 1 $\mu\text{m/s}$ and a critical coalescence speed of 100–200 $\mu\text{m/s}$. In this speed range, Marangoni effects play a significant role in the film stability. The observed patterns driven by surface tension gradients are similar to those observed in films of volatile pure organic liquids formed under free evaporation conditions.² Volatile pure organic liquids generally do not form films under vapor saturation at a temperature above the surface freezing point³

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while they do form films under free evaporation conditions, due to tension gradients caused by evaporative cooling that have a stabilising effect because they drive fluid circulation into the film.²

As a sequel to our previous paper on water films observed under water vapor saturation,¹ we have investigated water films under evaporation conditions. We describe the influences of slight local changes of temperature caused by evaporative cooling, as well as the effects of trace amounts of surface active impurities. Comparing the optical features of water films under vapor saturation and those in evaporation, we discuss Marangoni drag and drainage effects induced by surface tension gradients.

2. MATERIALS AND METHODS

Water was deionized by reverse osmosis (Microline, USA) and ion exchange (LiquiPure LS LBDR01202, USA) followed by sub-boiling distillation in the same manner as in the previous paper.¹ The resulting water had pH of 5.8 and conductivity in the range 0.5 – 1 $\mu\text{S}/\text{cm}$. Sodium chloride (ACS reagent, Sigma-Aldrich) was recrystallized before use.

The Mysels-Scheludko type film balance^{4,5} employed in this work has been described in previous papers.^{1,2} The apparatus can measure the film thickness and visualize complex patterns of chaotic flow in turbulent liquid films resulting from Marangoni effects while measuring disjoining⁶ and viscous-drag pressure (Figure 1). A sodium lamp was used as a monochromatic light source to visualize optical film features. Film thicknesses were calculated from the reflection intensity based on a single-layer model.^{5,7} High interference contrast at normal incidence permitted detection of trace organic contamination at monolayer levels. An organic layer just a few nm thick on a ~ 100 nm thick water film was observed as domains with a difference in reflectivity of $\sim 1\%$.

Water films were formed in the supporting ring (Fig. 1) with the water introduced directly from the filling vessel in which the distillate was collected, while contaminants possibly residing on the inner walls of the instrument were progressively washed away from the ring where the water films were formed. This protocol was adopted as a standard procedure in studying stability that depended on the age of the film. The films in vapor saturation condition were investigated in a glass cell sealed with either a mica sheet (punctured to permit insertion of tubing) or an airtight Teflon[®] cover cap having a tilted window and tube inlets. Circulation of moist or dry air through the cell was optionally provided through these inlets. Evaporation rates under ambient conditions were measured by monitoring the weight of water in a Petrie dish stationed on an analytical balance.

3. RESULTS

3.1 The stability of pure water films

In our previous paper,¹ we reconfirmed that highly-purified water does indeed form stable films.⁸ However, as soon as water is exposed to an environment, its purity can be affected by anything from the environment, for example, slow release and adsorption of ionic contaminants from the apparatus, airborne molecular contaminants, or dust. We have investigated the effects of ageing on the stability of water films. Table 1 shows the conditions for film formation with various liquids. Under saturated vapor conditions, water films remain for hours and days without changing their thickness, in contrast to electrolyte solutions and volatile organic liquids which do not form films in saturated vapor.^{1,2} The water films remain optically uniform (Fig. 1) and the brightness of light reflected from them does not change over several days. These observations indicate that the stability of a distilled water film is not affected by ageing under saturated vapor.

When the same experiments were carried out in free evaporation conditions, i.e., in low-humidity air, the water film was clearly affected by ageing. A film formed from aged water (typically 12–48 hours after distillation), which was initially optically bright with a thickness of about 150 nm, gradually darkened (indicating thinning) in the film region (Figure 2). Figure 3 shows film thinning of water at 12 hrs and 48hrs after distillation as a function of drainage time. The films were observed to break in a minute or so, thinning below a critical rupture thickness of ~50 nm in the central area. It was noted that films from older water (48hrs compared to 12hrs for example) tend to have shorter drainage time. It was also noted that the older films thinned more asymmetrically. This suggests that the purity of water continuously decreased with time. A period of thinning to coalescence of about 1 min in aged water films was similar to that observed for NaCl solution (8×10^{-4} M) films in vapor saturation.¹ However, the dynamic thickness-modulation pattern of aged water films in evaporation (Fig. 2) was distinctly different from the one observed with electrolyte solution films in vapor saturation, which continuously drain without reaching equilibrium thickness, developing an asymmetric cylindrical wedge.¹ When films were kept in saturated vapor for 2–3 days and then the ambient condition was changed to free evaporation by an abrupt reduction of relative humidity, the films thinned locally to a critical rupture thickness within a minute (Figure 4).

By contrast, a film formed from fresh water maintained the same brightness as it had in vapor saturation for at least several minutes after switching to a low humidity environment, and typically for an hour. Thin films of fresh water maintained constant thickness for several minutes to over an hour even when films were exposed to a laminar flow of dry nitrogen or air. This observation reveals that the stability of a water film in free evaporation is affected by ageing. Because of this, one could qualitatively evaluate the purity of water by observing the lifetime of a water film under evaporation conditions.

Here, we would like to stress that the types of distilled water discussed above (both fresh and aged) are readily distinguishable from less carefully-prepared (conventional) water in film lifetime and the film profile revealed by optical reflectivity. In comparison with the distilled waters discussed above, we investigated distilled water that had been stored for several days; filtered (demineralised and deionised “MilliQ®”) water; and tap water. Films formed from more than 3 day-old distilled water were also optically uniform under vapor saturation; however, once exposed to free evaporation conditions by admitting dry or moist air into the apparatus, a small but distinct change in reflectivity indicative of surface condensation of organic contamination often started appearing on the uniform optical density background of the surrounding clean water (Figure 5). The initially sub-micron size figures, similar to that of a surfactant monolayer spread on a Langmuir trough, grew in size while remaining mobile in the film, and joined together into larger islands with fractal outlines. With filtered water films, the figures started appearing in a shorter period than with several day-old distilled water. Tap water films collapsed so quickly that no optical features were able to be observed.

3.2 Water films in fast drainage

In the previous section, we described the optical appearance of films formed quasi-statically: two air-water interfaces were brought together at an approach speed less than 1 $\mu\text{m/s}$. We have also investigated optical features of films formed dynamically. As reported previously,¹ only transient films were formed when two air-water interfaces were brought together at speeds of 1–100 $\mu\text{m/s}$ in saturated vapor. Lifetimes of the transient films decreased from 100 s to 10 s with increasing approach speed from several $\mu\text{m/s}$ to a critical speed (which was in the range 100 – 200 $\mu\text{m/s}$, with the value increasing in more aged water) above which two air-water interfaces coalesced instantly.¹ Figures 6 and 7 show interferometric images observed in transient films formed when the two interfaces

approached at just below the critical speed. As the surfaces approached they deformed in a classic dimple,^{9,10} forming a rapidly expanding film whose shape is that of a convex water lens, thicker at the center than at the edges. The convex lens evolved to a pseudo-droplet (a droplet floating in the surface of liquid) about 1 μm thick in the center trapped between the two air-water interfaces (Fig. 6). When the film expansion slowed down, the pseudo-droplet remained in the film without change for 3 – 20 seconds and moved towards the meniscus. After several more seconds, the droplet suddenly formed a new connection to the meniscus (Fig. 7a–b). A series of meniscus connections proceeded to form one by one at intervals of about 1 s, resulting in a characteristic star-like pattern (Fig. 7c–d). Each new connection noticeably randomised the flow by affecting the other streams. The drainage was observed to become chaotic at this stage (Fig. 7e–f). Fig. 7f was captured just before the film collapsed.

The critical speed above which the two air-water interfaces instantly coalesce without forming the transient film is not affected by relative humidity (evaporation rate) but is affected by ageing of the water. The critical speed observed in free evaporation was the same as in vapor saturation, while aged water has a critical speed higher ($\sim 200 \mu\text{m/s}$) than fresh water ($\sim 100 \mu\text{m/s}$).

4. DISCUSSION

4.1 Mechanism of film formation with evaporation

How do films of freshly filled water undergoing continual evaporation maintain constant thickness over time? When the film thickness decreases by evaporation the disjoining pressure increases. The pressure difference ΔP between the thin flat part of the film and the meniscus around the film should induce continuous flow of water from the meniscus into the film in order to restore hydrostatic equilibrium shifted by the evaporation. The estimated rate of film thickening due to inward flow into the film even with the maximum pressure difference is about 1 nm/s or less (Appendix A). The thickening rate must be equal to the evaporation thinning rate in order to maintain constant film thickness. However, the rate of thickening associated with pressure-driven inward flow is at least 2 orders of magnitude slower than the water evaporation rate which was measured to be 0.1 $\mu\text{m/s}$ in this experiment. Hence the viscous drag theory suggests that flow caused by the pressure difference does not produce water flow from the meniscus into the film fast enough to maintain the observed constant thickness in evaporation.

To find a reasonable explanation, we note that a surface tension difference $\Delta \gamma$ between film and the meniscus^{11,12} is caused by the evaporation. The surface tension of the film area should be slightly higher than that of the meniscus because the film, which has a low mass and inhibited heat transfer, cools faster than the meniscus in evaporation. The film-meniscus tension difference $\Delta \gamma$ caused by cooling is estimated to be 0.1 – 0.2 mN/m,^{2,13} which is about ten times larger than the maximum possible effect of disjoining pressure. The $\Delta \gamma$ caused by cooling actively assists the inward drag of the liquid from the meniscus into the film. The surface stress boundary condition suggests that the inward flow velocity created by temperature difference between film and meniscus is fast enough^{13,14} to supply water lost by evaporation (Appendix B). Thus the cooling effect provides an explanation for water flow into the film to match the evaporation rate so that the equilibrium thickness is maintained.

The cooling effect, which induces chaotic circulation in volatile organic films, will be discussed in the following section where we compare this with chaotic flow in aqueous electrolyte films.

4.2 Influence of impurities on film stability with evaporation

Under evaporation conditions, impurities are transported into the film by the evaporation-induced flow of water from the meniscus into film. They are also concentrated directly by the solvent loss from the film due to evaporation, if the film is thinning on a time scale shorter than solute diffusion into the film. The concentration of impurities within the film increases several times in just 10 s according to an estimation based on the evaporation rate and the ratio of meniscus and film areas (Appendix C).

For organic compounds and surfactants as well as for pure-water electrical double layer (hydroxyls with charge-compensation cations),¹⁵ adsorption is essentially positive. The accumulation of such positive surface activity components decreases the film surface tension below the surrounding meniscus value (Fig. 8a). As the developing tension gradients cause water to flow out from the film to the meniscus until the film breaks, generally adsorption of positive surface activity components destabilise water films through evaporation-enhanced Marangoni-driven drainage. Note that the decrease of surface tension caused by adsorption is much more significant than the increase of surface tension by evaporative cooling.

An increase in concentration of negative surface activity components such as electrolytes transported into the film by evaporation increases the film surface tension, as does the evaporative cooling effect. When the concentrations of electrolytes are less than 10^{-5} M at the start of evaporation, the contribution of the trace impurity electrolyte to increase the film surface tension is not pronounced because the increase of surface tension by the concentration change is less significant than the increase of surface tension by evaporation cooling. Under evaporation, the electrolyte concentration in the film could be increased from 10^{-5} M to $\sim 10^{-3}$ M in 100 s (Appendix C). Under vapor saturation, such a film would not form because the maximum disjoining pressure at this electrolyte concentration would decrease to below the capillary pressure $2\gamma/R_c$ (in which γ is surface tension and R_c is the radius of the film balance capillary; however, we observed that the film remained stable in evaporation (Table 1). This could be interpreted as either (i) the concentration of the film did not reach 10^{-3} M due to residual convection, or (ii) the hydrodynamic repulsion associated with cooling and the salt-concentrating effect that develops Marangoni-driven inward flow becomes more dominant than the diminishing electrostatic repulsion.

We also observed films of 10^{-1} M NaCl aqueous solution stabilised in evaporation by continuous steady circulation (appearing as vortices)¹⁶ similar to that observed with volatile organic solvents² (Table 1). As the solute concentration in the film could initially increase ten times in 10–30 s depending on the film thickness (100–300 nm) with a water evaporation rate of $0.1 \mu\text{m/s}$ (Appendix C), the surface tension in the film should become high enough to enhance water flow into the film. Lessard and Zieminski observed higher turbulence in higher NaCl concentration.¹⁷ The estimated surface tension difference $\Delta\gamma$ between film and meniscus is about 1 mN/m. It is interesting to note that this value is the same order as the estimated $\Delta\gamma$ of volatile organic solvent films in evaporation,² suggesting that continuous steady circulation is caused by $\Delta\gamma$ between film and meniscus in both cases. The surface tension difference is caused by concentrating electrolytes in the film when the film medium is electrolyte solution, and caused by cooling when the film medium is volatile organic solvent.

4.3 Chaotic flows in rapidly expanded films

Water films formed with an approach speed of the two air-water interfaces just below the critical collision speed develop chaotic flows in the film (Fig. 7). The drainage patterns show several features in common with those observed in volatile organic solvent films and in aqueous electrolyte films formed statically (approaching speed $< 1 \mu\text{m/s}$) in evaporation.

Under dynamic conditions, centrifugal flow caused by film expansion pushes an adsorbed layer of positive surface activity components (hydroxyls with charge-compensation cations, organic contaminants) in the film toward the meniscus (Fig. 8b). The sweeping out of the adsorbates that creates new (therefore clean) surface at the center by the film expansion increases the surface tension in the middle of the film. Consequently, water at the perimeter of the film starts flowing back toward the middle, creating a thicker central area. The inward flow induces a thinner “moat” portion separating the thicker central area from the meniscus. The pseudo-droplet (formed between dimpled profiles on both surfaces of the film) that forms in this way (Fig. 6) maintains the tension balance between center and perimeter of the film while the film is expanding. After the film radius stops increasing, the pseudo-droplet moves toward the meniscus while decreasing in thickness because the transient mechanical equilibrium which maintained the pseudo droplet in the middle of the film is easily collapsed with minor asymmetries created by Marangoni convection (Fig. 7a). Figure 9 shows the flow motion probed by a Teflon[®] particle (~50 μm diameter) during formation of a mild pseudo-droplet on the film surface. It demonstrates that the flow was centrifugal at the beginning (Fig. 9a–b) but turned inward (Fig. 9b–d) until the pseudo-droplet expanded at the meniscus (Fig. 9d–f). It was noted that the Teflon particle was not observed to dramatically affect film stability, in contrast to the observed effects of positive surface activity contaminants. This could be because the Teflon particle was not in water but floating at the air-water interface. It could also be explained by the lateral force from the flow created by surface tension gradients preventing the Teflon from acting as an initiator of film rupture. The Teflon tracer neither induced film collapse nor thinning, consistent with the use of particle tracers to aid visualization of flows in liquid films²⁰.

As the pseudo droplet moves closer to the meniscus, the surface tension gradient between the pseudo droplet and the meniscus becomes steeper, and eventually creates a channel streaming liquid from the droplet to the meniscus (Fig. 7b). The channel is formed instantly, looking similar to a 2D analogue of ordinary coalescence of two droplets. However, unlike the case with ordinary coalescence in 3D, in which the channel immediately widens to fuse two droplets into one, it is prevented from widening in this case due to the region of lower surface tension (the “moat” portion) outside the channel remaining thin. The channel generally remains until the film breaks, as observed in Fig. 7c–f.

5. CONCLUSIONS

We have reported how the stability of water films depends on the condition of the water. Minor impurities do not affect the lifetime of water film under vapor saturation, but significantly influence the stability in free evaporation because impurities are transported into the film by the evaporation-induced flow of the water from the meniscus into the film. When the impurities are positive surface activity components such as organic compounds, water films are destabilized as the surface tension in the film is decreased by the impurities, causing outward Marangoni flow. In contrast, negative surface activity components such as electrolyte stabilize water film due to the increase of surface tension in the film, resulting in inward Marangoni drag.

The most dominant factor of transient film stabilization in dynamic conditions under evaporation is a surface tension gradient created in the films. For a distilled water film, the surface tension gradient is caused by evaporative cooling. For electrolyte films, it is caused by the difference of electrolyte concentration between film and meniscus. For a rapidly expanding film, centrifugal flow creates the surface tension gradient.

Since the surface tension gradient is enhanced by impurities, surface elasticity of a film with impurities is higher than that of pure water. Consequently, the critical collision speed is

increased with increasing concentration of impurities.^{1,18} Our observation is consistent with the reported observation that minute amounts of impurity delay the on-impact coalescence of water droplets falling on a water pool.¹⁹

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APPENDIX A

From Reynolds drainage theory for parallel disks of radius r_d , the rate of thickness change is $V_z = \Delta P h^3 / 3 \eta r_d^2$, in which ΔP is the pressure difference between the film and surrounding fluid; h is film thickness, and η is viscosity. With the following values appropriate to our experiment, $h = 200\text{--}100\text{ nm}$, $\Delta P = 100\text{ Pa}$, $r_d = 0.5\text{ mm}$, and $\eta = 0.0009\text{ Pa}\cdot\text{s}$, V_z is calculated to be $1.2\text{--}0.15\text{ nm/s}$.

APPENDIX B

In evaporative conditions, the surface stress balance condition is expressed as $\eta(dV_r/dz) = -(d\gamma/dT)(dT/dr)$, where dV_r/dz is the gradient of radial velocity perpendicular to the surface, $d\Delta\gamma/dT$ is the temperature coefficient of surface tension (0.2 mN/m/K), and dT/dr is the radial temperature gradient between the meniscus and the film.^{12,13} Taking parameters from our experiments: temperature difference between the meniscus and the film ($\cong 1\text{ K}$), distance between film center and middle of the meniscus $r (= 1.7\text{ mm})$, average thickness in the meniscus region ($z = 10\text{ }\mu\text{m}$), the estimated V_r is 1.3 mm/s , which is consistent with the reported flow rate accomplished with surface temperature perturbation less than 1 degree .¹³ The loss of water volume by evaporation in the film is about $10^{-4}\text{ mm}^3/\text{s}$. The calculated volume of water flowing into the film with the estimated V_x is of the same order as the volume loss by evaporation.

APPENDIX C

The concentration C_t in the film at time t can be expressed as

$$C_t = \sum_{i=1}^t \frac{C_{t-1} V_0 + C_0 dV_{\text{in}}/dt}{V_0 - dV_{\text{drain}}/dt}$$

in which V_0 is initial film volume, C_0 is initial solute concentration, dV_{in}/dt is flow rate from meniscus to film ($\cong$ evaporation rate), and dV_{drain}/dt is drainage rate. Putting $C_0 = 10^{-5}\text{ M}$ and $V_0 = 2 \times 10^{-12}\text{ m}^3$ (for a film thickness 300 nm and film radius 1.5 mm), $dV_{\text{in}}/dt = 7 \times 10^{-13}\text{ m}^3$ (corresponding to the measured evaporation rate of $0.1\text{ }\mu\text{m/s}$), $dV_{\text{drain}}/dt = 7 \times 10^{-15}\text{ m}^3$ (corresponding to thinning at nm/s), gives $C_{30} = 10^{-4}\text{ M}$. For the case of $V_0 = 7 \times 10^{-13}\text{ m}^3$ (film thickness 100 nm , film radius 1.5 mm), we find $C_3 = 3 \times 10^{-5}\text{ M}$, $C_{10} = 10^{-4}\text{ M}$, and $C_{100} = 1.7 \times 10^{-3}\text{ M}$.

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Figure 1.

A schematic drawing of the film balance (top) and an optical reflection image of a water film formed with 'fresh' distilled water in free evaporation (bottom). Inner diameter of film holder is 4 mm, and water film diameter in this case is 1.8 mm.

Figure 2. Optical features of a film formed from 'aged' water (12 hours since distillation) observed in free evaporation (top) and the thickness profiles (bottom).

Figure 3. Thickness changes of films formed from ‘aged’ waters in free evaporation, under a negative hydrostatic pressure of ~ 70 Pa; 12 hours since distillation (open diamonds), and 48 hours since distillation (filled circles).

Figure 4.

This image of a water film maintained in the film holder for several days at vapor saturation was taken about a minute after admitting dryer air into the cell, several seconds before the coalescence collapse. The combined effect of stray trace adsorption and evaporation induces the Marangoni drainage from the thinning (darker) inner areas toward the periphery of the film. The more progressed dimple on the left hand side ultimately breaks the film on reaching a critical thickness of less than 40 nm.

Figure 5.
Optical features of films formed from distilled water more than 3 days old, observed after exposure to free evaporation conditions.

Figure 6.

A pseudo-droplet (dimple) forming between the surfaces mutually approaching at a $150 \mu\text{m/s}$. Film thickness variation between two adjacent maximum and minimum intensity lines is 147 nm.

Figure 7.

Interference images of flow in a water film rapidly expanded to a large area. The last image (f) is taken at an age of 29 seconds, several seconds before the collapse. Film radius 1.6 mm, ring diameter 4.3 mm; continued series of experiments using same water as in Fig. 6. The bar is 1.0 mm. Initial thinning speed was $80 \mu\text{m/s}$.

Figure 8. Schematic drawings of film thinning with positive surface activity components in relatively static condition (a) and dynamic condition (b). Arrows show flow directions and arrow heads show rupturing points.

Figure 9.

Flow monitored by a Teflon[®] particle used as a probe (circled in white) during formation of a mild pseudo-droplet on the film surface. The origin coordinate (0,0) corresponds to the centre of the film. Initial thinning speed was 10 $\mu\text{m/s}$.

Table 1

Features of films at constant hydrostatic pressure (quasistatic thinning). Previous results from References 1 and 2 are included for completeness.

film media	vapor saturation			free evaporation ***		
	life time	film thickness	film features	life time	film thickness	film features
distilled water 'fresh'	hours-days ^{1, *}	50-300 nm ¹	optically uniform stable thickness ¹	several minutes-hours	50-300 nm	optically uniform stable thickness (Fig. 1)
distilled water 'aged' (typically 24-48hrs)	hours-days [*]	50-300 nm	optically uniform slight thinning	less than a minute	thinning from 150 nm to 50 nm	thinning from the central area (Fig. 2)
electrolytes ([NaCl] >1mM)	less than 40 ms	coalescence distance 50 nm	no film	depends on salt concentration	1 mM similar to above	1 mM thinning (concave)
					0.1 M similar to organic liquid films	0.1 M vortex ¹⁶
Organic solvents (ethanol, chloroform, n-pentene ^{***2})	less than 40 ms		no film	depends on relative vapor pressure		vortex ²

* After days, freshly formed film inevitably becomes aged film

** Above surface freezing point

*** Free evaporation: distance between air-water interfaces decreased at about 0.1μm/s