Drainage mechanism of microbubble dispersion and factors influencing its stability

Wanhua Feng\textsuperscript{a}, Naresh Singhal\textsuperscript{a,}*, Simon Swift\textsuperscript{b}

\textsuperscript{a} Department of Civil and Environmental Engineering, University of Auckland, Auckland, New Zealand
\textsuperscript{b} Department of Molecular Medicine and Pathology, University of Auckland, Auckland, New Zealand

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\textbf{A B S T R A C T}

Microbubble dispersion stability is a desirable characteristic in applications such as separation processes and in-situ bioremediation. This study investigates the effects of surfactant concentration, pH and ionic strength on the stability of dispersions of rhamnolipid, a common anionic biosurfactant. Microbubble dispersions of rhamnolipid and the non-ionic synthetic surfactant tergitol 15-S-12 were prepared by intensive stirring at 8000 rpm with solutions of 500–4000 mg l\(^{-1}\) surfactant concentration at pH 6–8. The ionic strength tests were performed with 1000–3000 mg l\(^{-1}\) sodium chloride. Dispersion stability increases for higher surfactant concentrations, but decreases with rising pH and increasing salt concentration. However, increasing the pH in the co-presence of salt enhances dispersion stability. A modified model showing improved fits to liquid drainage from the dispersions is presented and it is shown that liquid drainage occurs in three distinct phases, instead of two phases as previously assumed in the literature.

1. Introduction

Microbubble dispersions are suspensions of minute spherical gas bubbles encapsulated by a soapy liquid film in an aqueous surfactant solution [1,2]. The small size of the bubbles (25–100 \(\mu\)m) gives them colloidal properties and so the dispersion is also termed colloidal gas aphron [1,3]. The hypothesized structure of a microbubble comprises of a gas core encapsulated by multiple layers of surfactant molecules, which retard coalescence of the microbubbles, thereby giving it remarkable stability compared to conventional bubbles [4]. This feature coupled with a large interfacial area arising from the small bubble size has resulted in its applications in separation processes [5–9]. It has been suggested that microbubble dispersions can enhance bioremediation by effectively increasing mass transfer of oxygen and nutrients in the subsurface [10–12].

The stability of microbubble dispersions is a critical property with implications for the above discussed applications [2]. In conventional aqueous foam the stability is determined by the rate at which liquid drains from foam and the rate of foam break down [13]. However, in microbubble dispersions liquid drainage rate is the principle parameter determining stability because no perceptible breakdown of bubbles takes place prior to the majority of liquid being drained from dispersion [14]. Three main process parameters (surfactant and electrolyte concentrations and pH) have shown to have significant effects on dispersion stability. In general, increasing the surfactant concentration raises the dispersion stability [3,15,16], but increasing the electrolyte concentration has an adverse effect on the stability. The reported effects of pH on microbubble stability have been inconsistent with some studies showing no effect [16–18] and others reporting a strong, but complex, dependence on pH [19]. For example, the dispersion stability of cationic surfactant TTAB increased as pH was raised from acidic to neutral conditions, but then sharply decreased when the pH was made alkaline [19]. Reasons for such inconsistent behavior have not been adequately discussed in the literature.

Microbubble dispersions resemble emulsions and it has been suggested that their drainage mechanism differs from conventional foams, the latter typically exhibiting an exponential decrease in drainage with time [4,13,17,20]. The drainage of microbubble dispersions has been described in terms of microbubbles rising as per the Stroke’s velocity [19] or a two-stage process consisting of an initial stage during which liquid drains under gravity followed by a stage in which foam breaks down due to thinning of films between bubbles [14,17]. However, the two-stage process is similar to the drainage mechanisms proposed for conventional wet foams [20–22]. These conceptual models for the drainage of microbubble dispersions in the current literature appear to be incomplete and do not provide a satisfactory explanation for the observed differences between the drainage curves for microbubble dispersions and conventional foam.

Previous characterization studies have primarily been conducted using microbubble dispersions of synthetic surfactants.
Studies with microbubble dispersions prepared from natural surfactants or from mixtures of surfactants have been limited. Such studies may potentially have a significant impact as studies with dispersions of saponin, a plant-based natural surfactant show that these are more stable than those of synthetic surfactant SDS [23] and that dispersions of combined synthetic surfactants can remain stable for days [11]. In addition, biosurfactants such as rhamnolipid, a rhamnose-containing glycolipid surfactant produced mainly by Pseudomonas aeruginosa, have a lower environmental toxicity and are therefore preferable to synthetic surfactants in many industrial applications [24].

This study investigates the effects of biosurfactant concentration, solution pH, and electrolyte concentration on the stability of rhamnolipid microbubble dispersions relative to the non-ionic chemical surfactant Tergitol 15-S-12. In addition, the study expands on the mechanisms of microbubble dispersion drainage to fill the gap in current understanding and presents a modified model showing improved fits to dispersion drainage data.

2. Materials and methods

2.1. Chemicals

JBR 425 (Jeneil Biosurfactant Co.), a 25% of rhamnolipid solution, was used to supply biosurfactants. Other chemicals used were the non-ionic synthetic surfactant Tergitol 15-S-12 (Sigma-Aldrich), sodium chloride (Scharlau), and concentrated NaOH and HCl (both from LabServ). Solutions of 1 M NaOH and HCl were prepared from the concentrated stock and used to change the solution pH.

2.2. Microbubble dispersion

The microbubble dispersion was produced by high-speed stirring following the method described by Sebba [1]. One liter surfactant solution with rhamnolipid concentrations of 500 mg l\(^{-1}\), 1000 mg l\(^{-1}\) and 4000 mg l\(^{-1}\) at pH 5, 6, 7 or 8 was mixed with air at 8000 rpm at room temperature (25 ± 2°C) and atmospheric pressure for 3 min. Dispersions with 1000 mg l\(^{-1}\) tergitol solution were similarly prepared. Where indicated, sodium chloride was added to achieve salt concentrations of 1000 mg l\(^{-1}\) and 3000 mg l\(^{-1}\). The viscosity of surfactant solution was measured using a Rheometer (PHYSICA UDS 200, Paar Physica) at a constant temperature of 25°C.

2.3. Bubble size measurement

A small sample of freshly prepared microbubbles was placed in a cavity glass slide under a light microscope (Nikon ECLIPSE E600) with 4× magnification. A digital camera (Nikon Digital Sight DS-U1) attached to the microscope was used to obtain photographs immediately after the microbubbles were prepared and then at 3 min intervals up to 30 min. The photographs were analyzed using the built-in Nikon software (Nikon Act2U) and MatLab (version 7.0.4) image analysis tool pack to obtain the mean bubble size as well as the bubble size distribution. About 100–300 bubbles were counted for each sample.

2.4. Stability measurement

Microbubble dispersions were filled in 100 ml measuring cylinders to measure liquid drainage from the dispersion. Volumes of the drained liquid (\(V_L\)) and dispersion/foam phase (\(V_F\)) were recorded with time. The final volume of drained liquid (\(V_{\text{max}}\)) was recorded after the foam had completely collapsed. Each test was replicated six times by repeating the above procedure. The gas volume fraction of the microbubbles provided a measure of the amount of gas entrained in the microbubble dispersion and was expressed as the ratio of the gas volume (100 ml – \(V_{\text{max}}\)) to the total volume of the dispersion (100 ml). Following Sebba [1] the stability of the microbubble dispersion was quantified as the time taken for half the liquid to drain from the dispersion, i.e., the half-life (\(T_{1/2}\)). In addition to the liquid drainage profile, the foam volume fraction and liquid holdup within the foam phase are important parameters in understanding the drainage mechanism associated with the microbubble dispersion. Foam volume fraction is referred as the ratio of the foam volume (\(V_F\)) to total volume (\(V_F + V_L\)) [22]. Liquid holdup measures the volume fraction of liquid retained within the dispersion/foam phase and the average liquid holdup value can be approximated as the ratio of the liquid volume in the dispersion/foam phase (\(V_{\text{max}} - V_L\)) to the final drained liquid volume (\(V_{\text{max}}\)) [25].

3. Results and discussion

3.1. Microbubble characteristics

The initial mean bubble diameter and bubble volume fraction of the microbubble dispersion and the viscosity of surfactant solutions at various experimental conditions are presented in Table 1. In general, the solution viscosity increases with surfactant concentration, but pH does not have a significant effect on the solution viscosity. The initial mean bubble diameter of the microbubble dispersion varies between 63 and 71 μm, and is similar to the values reported by others [23,26]. Fig. 1 shows the size distribution of microbubble dispersion immediately after it was made from 1000 mg l\(^{-1}\) of rhamnolipid at pH 7. The majority of bubbles lie in the 20–140 μm diameter range.

The gas volume fraction in microbubble dispersion is fairly insensitive to the process parameters tested and only vary from 67% to 72%. These values are consistent with the range of 60–70% reported in the literature [4,18,27]. Other studies too have reported that the type of surfactants does not affect the gas volume fraction in microbubble dispersions [3]. Also, as the surfactant concentrations used in this study exceeded critical micellar concentration of the surfactant, the concentration would be expected to have little effect on the gas volume fraction [23].

3.2. Drainage kinetics

Liquid drainage curves of the microbubble dispersions follow an “S” shaped profile, with an increase in the rate of drainage at initial

<table>
<thead>
<tr>
<th>Surfactant concentration (mg l(^{-1}))</th>
<th>pH</th>
<th>Solution viscosity (cP)</th>
<th>Mean bubble diameter (μm)</th>
<th>Gas volume fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhamnolipid 500</td>
<td>6</td>
<td>1.52</td>
<td>70 (3)</td>
<td>71 (0)</td>
</tr>
<tr>
<td>Rhamnolipid 500</td>
<td>7</td>
<td>1.59</td>
<td>69 (4)</td>
<td>67 (2)</td>
</tr>
<tr>
<td>Rhamnolipid 500</td>
<td>8</td>
<td>1.61</td>
<td>70 (2)</td>
<td>68 (2)</td>
</tr>
<tr>
<td>Rhamnolipid 1000</td>
<td>6</td>
<td>1.62</td>
<td>67 (2)</td>
<td>72 (1)</td>
</tr>
<tr>
<td>Rhamnolipid 1000</td>
<td>7</td>
<td>1.76</td>
<td>71 (1)</td>
<td>71 (1)</td>
</tr>
<tr>
<td>Rhamnolipid 1000</td>
<td>8</td>
<td>1.77</td>
<td>63 (5)</td>
<td>68 (1)</td>
</tr>
<tr>
<td>Rhamnolipid 4000</td>
<td>6</td>
<td>2.03</td>
<td>64 (4)</td>
<td>69 (1)</td>
</tr>
<tr>
<td>Rhamnolipid 4000</td>
<td>7</td>
<td>1.96</td>
<td>61 (6)</td>
<td>69 (1)</td>
</tr>
<tr>
<td>Rhamnolipid 4000</td>
<td>8</td>
<td>1.93</td>
<td>65 (2)</td>
<td>69 (1)</td>
</tr>
<tr>
<td>Tergitol 1000</td>
<td>6</td>
<td>1.94</td>
<td>68 (4)</td>
<td>69 (1)</td>
</tr>
<tr>
<td>Tergitol 1000</td>
<td>7</td>
<td>1.93</td>
<td>70 (7)</td>
<td>70 (1)</td>
</tr>
<tr>
<td>Tergitol 1000</td>
<td>8</td>
<td>1.94</td>
<td>67 (4)</td>
<td>70 (1)</td>
</tr>
</tbody>
</table>
times followed by a decrease in the rate of drainage at later times (see Figs. 2(A) and 4). The observation is consistent with findings from other studies [14,28]. Liquid drainage with time from colloidal gas aphrons has been empirically modeled [14] as

\[ V_t = \frac{V_{\text{max}} t^n}{K_n + t^n} \]  

(1)

where \( V_t \) and \( V_{\text{max}} \) are the volume of drained liquid at time \( t \) and the final drained liquid volume, respectively, \( K \) is the half-life for liquid drainage and \( n \) describes the sigmoid character of the drainage curve. This model consistently under-estimates the drainage of liquid from rhamnolipid microbubble dispersions used in this study, as shown in Fig. 2(A) and (B) and so was modified by including a promotional term \((-t^n/K_n^{a-n})\) to give the following expression:

\[ V_t = V_{\text{max}} \frac{t^n}{2(K_n^{a-n} + t^n - (t^n/K_n^{a-n}))} \]  

(2)

On differentiating Eq. (2) the rate of liquid drainage is obtained as:

\[ \frac{dV_t}{dt} = V_{\text{max}} \frac{t^{a-n}K_n^{a-n}[(a-n)(t^n/K_n^{a-n}) + n]}{2(K_n^{a-n} + t^n - (t^n/K_n^{a-n}))^2} \]  

(3)

Detailed discussion of the modified model is available in the supplementary note. The modified model gives better fits to the measured data in comparison to original model in terms of smaller residual values as well as a more accurate prediction for the parameters of half-life and final drained volume (see Fig. 3). The values of \( n \) in the original model was found to depend mainly on the surfactant concentration [14]. The \( n \) and \( a \) parameters in the modified model also correspond well to the surfactant concentration at different pH values. In general, the parameters increase with increasing surfactant concentration as shown in Table 2.

3.3. Effect of rhamnolipid concentration on dispersion stability

Drainage curves for microbubble dispersions of rhamnolipid with surfactant concentrations of 500, 1000 and 4000 mg l\(^{-1}\) and...
pHs of 6, 7, and 8 are shown in Fig. 4 and the half-lives and final liquid drainage volumes are summarized in Table 2. No stable dispersions were produced at pH 5. Complete foam collapse occurred over approximately 2 h. Raising the surfactant concentration from 500 to 4000 mg l\(^{-1}\) led to increases in microbubble dispersion stability of 19–31% for pHs of 6–8. The increased stability at higher surfactant concentrations can be ascribed to several processes: increase in liquid viscosity from the presence of more surfactant molecules in solution, resulting in greater viscous drag that retards hydrodynamic film drainage between bubbles [29]; higher concentrations of surfactant molecules at bubble surfaces (i.e. the lamellar walls) that increase surface viscosity and elasticity [14,30], thereby enhancing bubble integrity by improving the mechanical strength of lamellar walls [29]; and, a decrease in bubble coalescence due to larger electrostatic repulsion between bubbles caused by the increase in rhamnolipid concentration [16,31].

### 3.4. Effect of pH on dispersion stability

Fig. 4 shows that the effect of surfactant concentration on the dispersion stability is more pronounced at higher pH (change by 30%) as compared to lower pH (change by 19%), indicating that the change in pH affects dispersion stability. To illustrate the pH influence in greater detail, the drainage behavior of microbubble dispersions at 1000 mg l\(^{-1}\) rhamnolipid and tergitol solutions for pH 6–8 is plotted in Fig. 5, and their corresponding half-lives are presented in Table 3. The stability of the dispersion from the anionic surfactant rhamnolipid decreases by about 10% for pH changing from 6 to 8, while that from the non-ionic surfactant tergitol remains unaffected, maintaining a half-life of approximately 390 s. The trend of decreased dispersion stability with increasing pH from 6 to 8 is also observed for other rhamnolipid concentrations (see Table 3).

The solution pH has been reported to have a significant influence on stability of dispersions of the cationic surfactant tetrade cyltrimethyl ammonium bromide (TTAB) [19], while the stability of dispersions of sodium dioctyl sulfosuccinate (AOT), an anionic surfactant, was unaffected for pH changing from 4 to 8 [16]. The different behavior of AOT and rhamnolipid dispersions, both of which are anionic surfactants, results from the differences in their degrees of ionization. The dissociation constants (pK\(_a\)) of rhamnolipid and AOT are 5.6 [32] and 2.9 [33], respectively. When pH is equal to pK\(_a\), half of the surfactant concentration gets ionized due to dissociation of the surfactant. In the 4–8 pH range, the dissociation of AOT increases marginally from 93% to 100%, while in the 6–8 pH range rhamnolipid dissociation changes from 70% to 100%, explaining the insensitivity in AOT stability to the change in pH.

Rhamnolipid anionization is principally due to the dissociation of its carboxyl head group (see Fig. 6) [34]. This causes greater electrostatic repulsion between adjacent ionized carboxyls, increasing the effective size of the head group [34] and reducing the concentration of rhamnolipid molecules at the bubble surface, thereby lowering the viscosity and elasticity of the bubble surface [14].

### Table 2

Comparison of observed and fitted half-life (\(T_{1/2}\)) and final drained liquid volume (\(V_{max}\)) values.

<table>
<thead>
<tr>
<th>Rhamnolipid surfactant concentration (mg l(^{-1}))</th>
<th>pH</th>
<th>Experimental data</th>
<th>(T_{1/2}) (s)</th>
<th>(V_{max}) (ml)</th>
<th>Model output</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>6</td>
<td>(547 \pm 12) (29 \pm 0)</td>
<td>481</td>
<td>31</td>
<td>1.513</td>
<td>0.9996</td>
</tr>
<tr>
<td>1000</td>
<td>6</td>
<td>(405 \pm 19) (28 \pm 1)</td>
<td>478</td>
<td>25</td>
<td>1.626</td>
<td>0.9995</td>
</tr>
<tr>
<td>4000</td>
<td>6</td>
<td>(546 \pm 13) (31 \pm 1)</td>
<td>538</td>
<td>31</td>
<td>1.557</td>
<td>0.9995</td>
</tr>
<tr>
<td>500</td>
<td>7</td>
<td>(405 \pm 13) (33 \pm 2)</td>
<td>387</td>
<td>33</td>
<td>1.243</td>
<td>0.9993</td>
</tr>
<tr>
<td>1000</td>
<td>7</td>
<td>(461 \pm 15) (29 \pm 1)</td>
<td>505</td>
<td>34</td>
<td>1.508</td>
<td>0.9997</td>
</tr>
<tr>
<td>4000</td>
<td>7</td>
<td>(519 \pm 18) (31 \pm 1)</td>
<td>529</td>
<td>31</td>
<td>1.565</td>
<td>0.9995</td>
</tr>
<tr>
<td>500</td>
<td>8</td>
<td>(385 \pm 13) (32 \pm 2)</td>
<td>387</td>
<td>33</td>
<td>1.327</td>
<td>0.9993</td>
</tr>
<tr>
<td>1000</td>
<td>8</td>
<td>(447 \pm 19) (32 \pm 1)</td>
<td>432</td>
<td>31</td>
<td>1.405</td>
<td>0.9994</td>
</tr>
<tr>
<td>4000</td>
<td>8</td>
<td>(503 \pm 11) (31 \pm 1)</td>
<td>473</td>
<td>28</td>
<td>1.578</td>
<td>0.9993</td>
</tr>
</tbody>
</table>
between adjacent bubble surfaces due to a compression of the double layer caused by the increase in ionic concentration of the solution [16,29]. However, at pHs 7 and 8 this effect is not observed as increasing the pH negates the effects of increasing the salt concentration. At higher pH, greater ionization of the rhamnolipid’s carboxyl group increases the electrostatic repulsion between rhamnolipid molecules, counteracting the lowering of repulsion caused by the higher electrolyte concentration. Additionally, the Na+ from the added salt shields against the effects of negative charge of the carboxyl head group, preventing an increase in the effective size of the head group at higher pHs [35], which could lead to reduced packing of the rhamnolipid molecules at the bubble surface as discussed in previous sections. The concentration of rhamnolipid molecules at the bubble surface is therefore maintained, and the combination of the above interactions stabilizes the microbubble dispersion.

3.6. Drainage model for microbubble dispersions

A typical “S”-shaped drainage curve and the drainage rate, obtained as the time derivative of the experimental drainage data are shown in Fig. 7. Based on the observed rate of drainage three phases can be identified—in the first phase the drainage rate increases rapidly with time, while in the second phase there is a sharp decrease in the drainage rate with time, and finally in the third phase the rate of drainage becomes relatively small. In earlier studies [14,17] the authors described the drainage process with only two distinct regions, with the first region primarily driven by gravity drainage and the second region by the thinning of films. However the two-staged drainage model does not provide satisfactory explanation to the “S” shape drainage curves observed both in this study and from previous studies [14,16,17,28].

Liquid drainage occurs invariably in foam and the rate of drainage is influenced by the initial distribution of the liquid between the film and plateau border [36,37]. During the first phase the drainage is a combination of liquid flow due to gravity through the plateau boarder and the upward creaming of microbubbles. While liquid drainage is a common process in aqueous foams [21], non-stirred dispersions, like emulsions experience the additional effect of creaming during which bubbles rise to the top driven by buoyancy forces resulting from density difference between the liquid and gaseous phases [22,38]. Also, in microbubble dispersions, larger bubbles increase in size with time due to disproportionation, whereby gas diffuses from the smaller bubbles (with greater internal gas pressure) into larger bubbles (with lower internal gas pressure) [4]. The growth of bubble size and the liquid in the third phase the rate of drainage becomes relatively small.
drainage are correlated [36,39]. As more liquid drains away the average bubble size becomes larger, which in turn leads to increased liquid drainage. Initially, as shown in Fig. 8A and Table 4, the microbubbles are spherical in shape with a mean diameter of 69 μm. Over time, the mean bubble size increases to 96 μm due to disproportionation as demonstrated by an expansion of the larger bubbles and the disappearance of smaller bubbles in Fig. 8A and B, and seen via the increase in 90 percentile bubble size in Table 4. As the creaming velocity increases with bubble size [38,40], the increase in bubble size causes the creaming velocity to increase with time during Phase I—a phenomena that has also been reported by others [41]. Creaming is hindered at higher emulsion concentration [40,42], and bubble expansion over time impedes the upward migration of other bubbles from the underlying region. Over time the liquid holdup and foam volume fraction gradually decreased, but no breakdown of microbubbles was observed and the total volume remained unchanged (Fig. 9).

The second phase starts when the dispersion loses its colloidal character due to bubble expansion and behaves similarly to conventional wet foam. Without continuous stirring colloidal gas aphrons will eventually separate into conventional foam [4]. Yan et al. [14] state that the formation of conventional foam occurs when 90% of the total liquid have been removed from the foam. However, Fig. 8B shows that the bubbles have expanded significantly and the larger bubbles are crowded and distorted at the end of Phase I, indicating that the microbubble dispersion has lost its colloidal character. In this region the dominant drainage mechanism is gravity-driven liquid flow through a plateau border network [22,39]. From Fig. 7 the timescale of plateau boarder drainage (∼1000 s), which dominates Phases I and II, is about 3–4 times larger than that for creaming (∼300 s), suggesting that plateau boarder drainage will occur over a substantially longer period of time than creaming. The continuous decrease in liquid content due to liquid drainage, as shown by the gradual decrease in the liquid holdup within the foam phase in Fig. 9, causes a steady drop in the rate change in bubble diameter over time.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Mean (μm)</th>
<th>90th (μm)</th>
<th>Reference in Fig. 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>69</td>
<td>110</td>
<td>a</td>
</tr>
<tr>
<td>360</td>
<td>92</td>
<td>176</td>
<td>b</td>
</tr>
<tr>
<td>1080</td>
<td>239</td>
<td>377</td>
<td>c</td>
</tr>
<tr>
<td>1620</td>
<td>410</td>
<td>592</td>
<td>d</td>
</tr>
</tbody>
</table>

Fig. 9. Changes in foam volume fraction, liquid holdup and total volume with time for microbubble dispersion formed from 500 mg l⁻¹ rhamnolipid solution at pH 6. Open round symbol represents foam volume fraction; open triangle symbol represents liquid holdup; and solid square symbol represents total volume. Arrows indicate corresponding axis.

Fig. 8. Photomicrographs of the microbubble dispersion at different times. Photo A represents T = 0 s; B represents T = 360 s; C represents T = 1080 s; and D represents T = 1620 s.
of drainage. This process is accompanied by the expansion of bubbles and the thinning of films (see Fig. 8B and C). The bubbles have changed from spherical to polyhedral in shape. During Phase II the mean bubble size increases from 92 to 239 μm (Table 4), but, as in Phase I no perceptible bubble collapse was observed and the total volume remained unchanged (see Fig. 9). The end of Phase II at about 1000 s is accompanied by a flattening of the decrease in liquid holdup with less than 10% of the liquid being retained in the foam phase (see Fig. 9). The half-life of microbubble dispersion from liquid drainage data is estimated as 457 s (see Table 2). The timescale of microbubble stability (~2 × 457 s) is therefore consistent with the timescale for removal of the majority of liquid (~1000 s) by the end of Phase II, at which time the foam converts from a wet to dry foam, initiating the third phase.

In Phase III the drainage of liquid is primarily from lamellae (films) under the influence of a plate on the boarder suction, which is a much slower process [14,21]. As shown in Fig. 8C and D the bubbles are polyhedral in shape and continue to expand in conjunction with the thinning of films. The bubbles now have an average size at least 3 times larger than those in Phase I (Table 4). Since the timescale of film drainage is much smaller than that of plate border drainage [43], the film drainage will attain equilibrium over a short time interval [36]. This is evident by the flattening of liquid drainage profile and drainage rate in Fig. 7 and stabilized liquid holdup within the foam in Fig. 9. With the removal of more than 90% of the liquid from the foam and the thinning of the films, bubble coalescence due to rupturing of films and eventually the foam phase starts to collapse, and is manifested as a gradual decrease in total volume (Fig. 9) after about 1000 s. A complete collapse of foam was observed about 2 h after the start of experiment. The equation developed for the rate of drainage (Eq. (3)) fits the observed data well in all three phases.

4. Conclusions

The stability of microbubble dispersions is a function of factors such as surfactant concentration, pH, and salt due to their influence on liquid viscosity and viscous drag, mechanical properties of lamellar walls, and bubble coalescence. Increasing the surfactant concentration enhances dispersion stability, particularly at higher solution pH. Higher pH results in greater ionization of the surfactant’s functional group, which can enhance or lessen dispersion stability, depending on the effect of ionization on bubble charge density and the repulsion between bubbles. In a similar way, an increase in electrolyte concentration (e.g., by salt addition to solution) can lower foam stability by compressing the electric double layer. This effect can, however, be counteracted by increasing the pH.

The drainage of microbubble dispersion is best described by three distinct phases instead of two phases as previously assumed in the literature. Initially, the drainage rate increases with time due to a combination of upflow migration of bubbles and downward liquid drainage under gravity. Following this phase, dispersion behavior is similar to conventional wet foam. Here the drainage rate decreases with time and is dominated by liquid flow under gravity. Eventually, the foam becomes water deficient and starts to behave like dry foam, where the drainage rate is small due to slow liquid release from films under capillarity suction. The modified drainage equation (Eq. (2)) provides better fit to the experimental results, and the derived drainage rate equation (Eq. (3)) corresponds well to the proposed three-phase drainage mechanism.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2009.05.054.

References