

1 **Relative contribution of cationic surfactant and counter-anion to a** 2 **liquid film tension**

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7 ***Abstract***

8 A model was developed to predict the bubble deformation in the presence of a charged surface.
9 The model was successfully verified with a bubble containing a cationic surfactant,
10 cetyltrimethylammonium bromide. The modelling results revealed that the film tension linearly
11 increased with the distance from the charged surface, due to the electrostatic repulsion of the
12 anions. More importantly, the analysis demonstrated that hydrated Br⁻ increased film tension,
13 whereas surfactant molecules reduced film tension. The anion's increment was estimated at ~ 14%
14 of the surfactant's reduction. The results verified the contrasting influences of surfactant and its
15 counter-ions on the tension of the air/liquid interfacial layer.

16 *Keywords: film tension, ionic interaction, cationic surfactant*

17 **Introduction**

18 Surfactants-stabilized foams are found in many industrial [1] and natural processes [2]. The
19 foaming fractionation process can be employed to separate the dissolved ions by interaction with
20 ionic surfactants [3,4]. In the literature, the interfacial adsorption of surfactant and counter-ion is
21 often simplified into a single dividing plane [5]. On the other hand, theoretical and experimental
22 studies have revealed different roles of surfactant and counter-ions within the interfacial zone. It

23 has been shown that ions are located further from the surface,[6] with a strong hydration shell [7]
24 and a lower frequency of H-bonds switching [8]. The hydrated counter-ions affect the surface
25 tension via their interaction with H-bond networks in the sub-surface layer [9]. The selective
26 impact of counter-ions on the surface layer has been well-documented for cationic surfactants [10],
27 such as C₁₄TACl/C₁₄TABr[11,12] and C₁₆TACl/C₁₆TABr [13]. The anions adsorption varies with
28 atomic size as well as water surface layer [7,14]. Similarly, the anionic surfactant can have
29 distinguished interactions with both monovalent [3] and divalent cations [4].

30 From these results, it can be hypothesized that the surfactant and counter-ion have unequal
31 contributions to the surface tension. In a recent simulation study, the contribution of surfactant and
32 counter-ion to surface tension was quantified separately [15]. It is fascinating to note that a cationic
33 surfactant, dodecyl trimethyl ammonium, and its counter-anion have opposite contributions to
34 surface tension. The unequal and contrasting contributions have a significant ramification on the
35 fundamental understanding and applications of ionic surfactants.

36 To quantify the individual impacts of counter-ions and surfactants, the interfacial layer needs to
37 be assessed at non-neutral conditions. The non-neutral conditions of the air/water surface have
38 been obtained under dynamic conditions. For instance, it has been demonstrated that the interfacial
39 layer can be divided into an “immobile” layer of hydrophobic tails,[16] and a “mobile” layer
40 dominated by the hydrated counter-ions. A simulation study also verified that the hydrate counter-
41 ions have much higher diffusivity than surfactant molecules [17]. The clearest evidence of the
42 multi-layers structure was obtained for the amphiphilic polymer at the air/water surface [18]. The
43 separation between these two layers at the air/water surface is often evidenced via the zeta potential
44 of small air bubbles [19]. However, these dynamic conditions are not suitable for surface tension

45 quantification. Furthermore, these investigations focuses on the air/water surface with a large bulk
46 liquid phase.

47 This study aims to generate and quantify the tension at a non-neutral and static state. Hence, we
48 focus on the thin film of a bubble, which is easily affected by an electrical force [20]. The local
49 non-neutral condition can generate a variable film tension, which then can be optically captured
50 and mathematically quantified via the classical Young-Laplace equation [21]. Ultimately, the
51 study aims to provide some quantitative measurements on the relative contribution of surfactant
52 and its counter-ion to the surface tension.

53 **Theory**

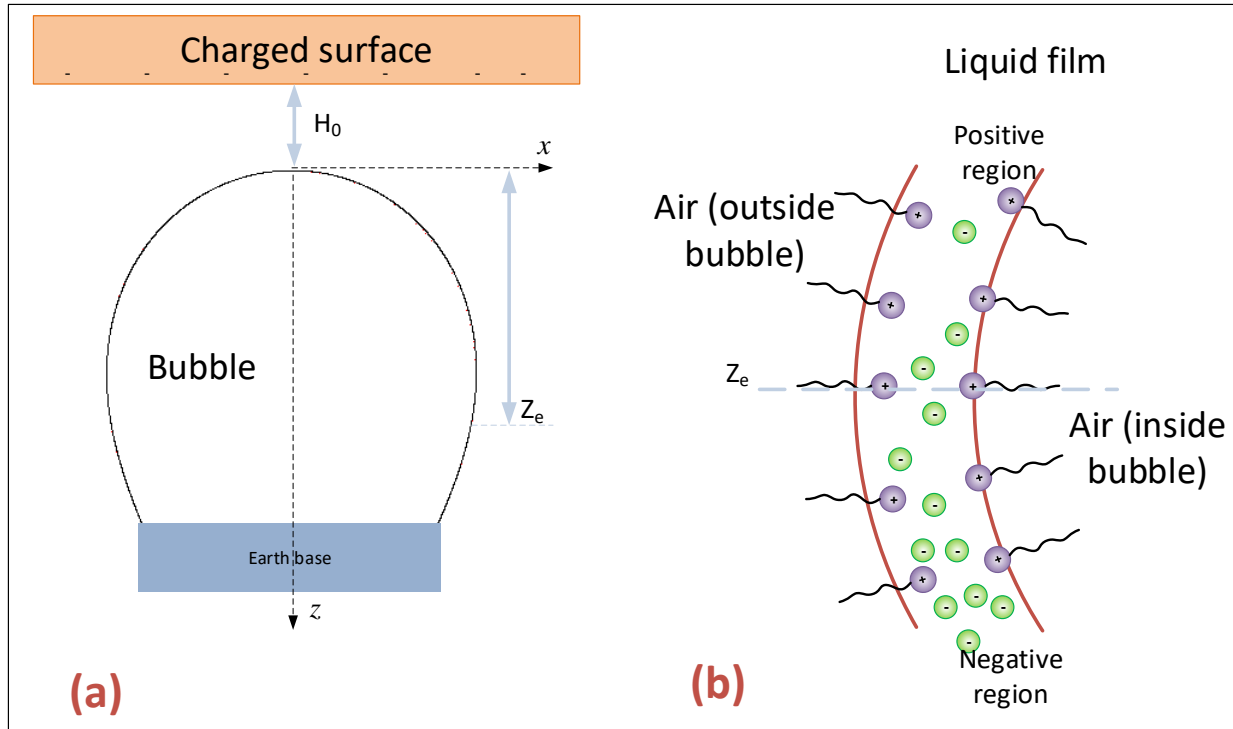
54 To obtain the static, and yet non-neutral, conditions of the surfactant layer, a bubble film was
55 employed under an electrostatic field (Figure 1a). A model is developed and solved numerically
56 for a bubble shape, which is deformed via non-neutral distribution within the film. The shape of
57 an axisymmetric interface can be described by a system of three 1st ODEs:[21]

$$58 \quad \frac{dx}{ds} = \cos \phi \quad (1)$$

$$59 \quad \frac{dz}{ds} = \sin \phi \quad (2)$$

$$60 \quad \frac{d\phi}{ds} + \frac{\sin \phi}{x} = \frac{\Delta P}{\gamma(z)} \quad (3)$$

61 Where s is arc length measure from initial point, ϕ is the tangent angle, γ is the interfacial tension
62 and ΔP is the pressure difference.



63

64 Figure 1. Bubble deformation under external electrostatic force (a) geometry of the bubble, (b) a
 65 non-uniform distribution of anions along z -axis.

66 The above system of ODEs has been solved for constant γ , producing shape-based methods for
 67 tension determination. The axis-symmetric interface can be a pendant or sessile shape in the
 68 conventional drop/bubble [22], or a holm shape for a large interface [23]. For the soap bubble in
 69 this study, however, the pressure difference is constant, and the tension is variable with z -axis
 70 (Figure 1b). In this instance, the thin liquid film is supported by the interfacial tension, instead of
 71 a solid frame as in the flat soap film [24]. The initial conditions of the above equations are defined
 72 at the apex of the bubble (when $x=0$ and $z=0$):

73

$$\phi_0 = 0 \quad (4)$$

74 In the absence of an external force, the film tension, γ_e , is uniform throughout the bubble shape,
 75 which is a part of a perfect sphere [25]. The value of γ_e is determined as twice of the surface tension
 76 [26].

77 In the presence of an external electrostatic field, the hydrated counter-ions are affected by the
 78 electrical force. On the other hand, the surfactant molecules are more immobile due to adsorption
 79 at the air/liquid surface. In the case of the electrostatic field from the surface of an insulator (Figure
 80 1), distanced at H_0 from the apex, the local acting force is inversely proportional to the distance,
 81 that is $z+H_0$. This force is balanced by electrostatic binding between the surface heads and counter-
 82 ions [27]. Hence, there is an ionic gradient in the z -axis. Since the film is neutral as the whole,
 83 there is a distance from the apex, Z_e , at which the thin film is neutral. At this distance, the film
 84 tension should be the same as γ_e . Above Z_e , the film is positively charged, that is having fewer
 85 counter-ions than surfactant head. Below Z_e , the film is negatively charged.

86 Since there is no prior model on the relationship between the local charge and film tension, we
 87 assume a linear correlation. Furthermore, the two correlations, below and above Z_e , should be
 88 different due to the unequal contribution of anion and surfactant to the film tension. Both
 89 correlations equal unity at $z = Z_e$. The equation satisfies these condition is given by:

$$90 \quad \frac{\gamma(z)}{\gamma_e} = (1-b_1) \frac{z+H_0}{Z_e+H_0} + b_1 \quad \text{for } z < Z_e \quad (5)$$

$$91 \quad \frac{\gamma(z)}{\gamma_e} = (1-b_2) \frac{z+H_0}{Z_e+H_0} + b_2 \quad \text{for } z > Z_e$$

92 Where b_1 and b_2 are the dimensionless constant for two regions.

93 It can be seen that when both b_1 and b_2 equal to 1, the above equation reduces to constant tension,
 94 that is $\gamma(z)$ equals to γ_e for the whole bubble. Substituting Eq(7) into Eq.(3), one has:

$$95 \quad \frac{d\phi}{ds} + \frac{\sin\phi}{x} = \frac{\Delta P}{\gamma_e} / \left((1-b_1) \frac{z+H_0}{Z_e+H_0} + b_1 \right) \quad \text{for } z < Z_e \quad (6)$$

$$96 \quad \frac{d\phi}{ds} + \frac{\sin\phi}{x} = \frac{\Delta P}{\gamma_e} / \left((1-b_2) \frac{z+H_0}{Z_e+H_0} + b_2 \right) \quad \text{for } z > Z_e$$

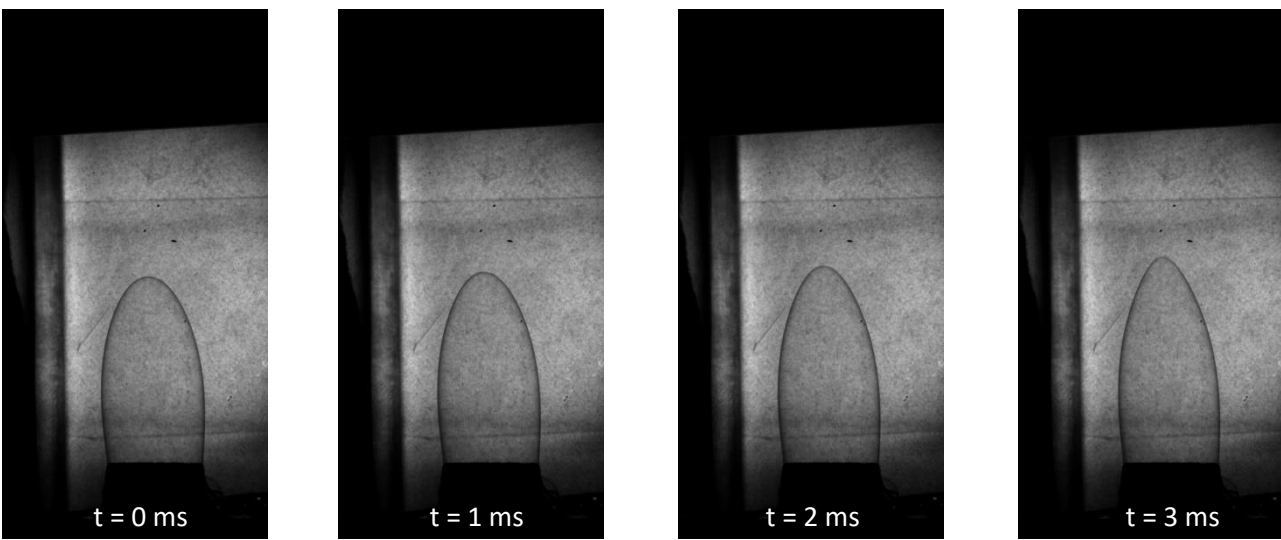
97 The system of Eq.(1), (2) and (6) can be solved simultaneously [28]. The obtained interface is
 98 fitted with the experimental images for different H_0 , which was directly determined from the
 99 experimental conditions. The value of $\Delta P/\gamma_e$ can be easily obtained from a non-charged bubble,
 100 which is a part of a sphere. Consequently, the model has three adjustable parameters: Z_e , b_1 and
 101 b_2 .

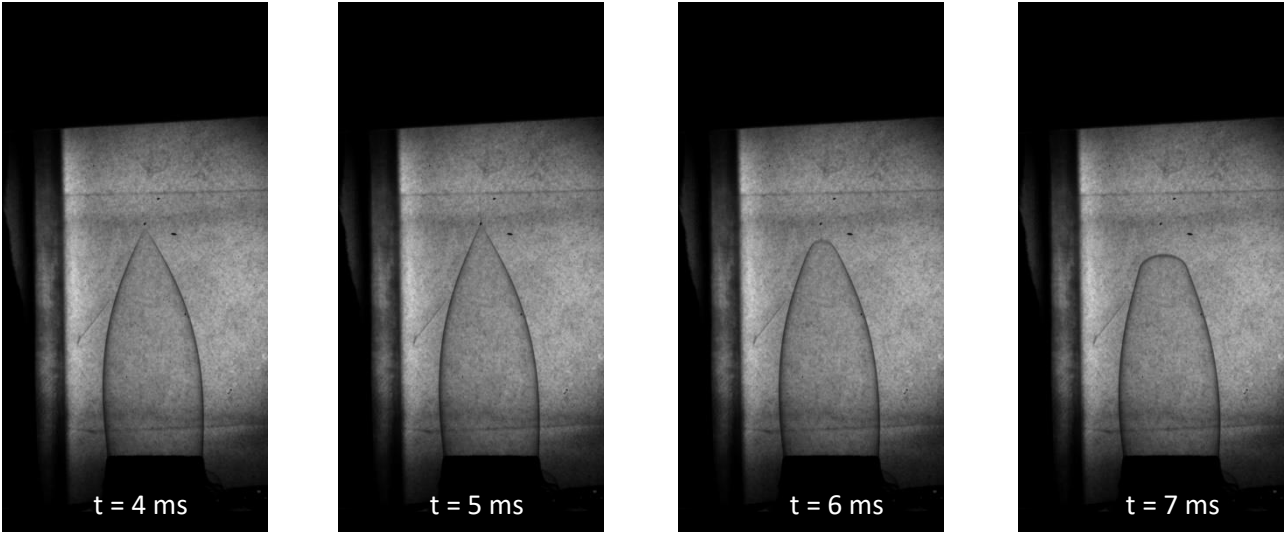
102 **Experimental**

103 Teflon was selected as the insulator due to its high surface triboelectric affinity, at -190 nC/J [29].
 104 The surface was charged by rubbing Teflon surface against a cloth. The electrostatic charge was
 105 verified by a surface voltmeter (SVM2, Alpha Lab Inc.). The saturated surface charge was obtained
 106 at -19.7 kV \pm 2%, with respect to the ground, at a distance of 2.54 cm. This value presents a static
 107 electrical field of 300 to 400 V/m, which is in a similar order of electro-driven interfacial
 108 deformation [30]. An aqueous solution of cetyltrimethylammonium bromide (CTAB) and glycerol
 109 was selected to stabilize the bubble during the deformation [31]. The surfactant concentration was
 110 twice the critical micelle concentration [32], at 2 mM. From a previous study, it was found that at
 111 low concentration, especially below CMCs, the soap film is very unstable and does not allow

112 effective observations [25]. Consequently, 2 mM was selected to ensure the film stability. The
113 glycerol concentration was kept at 10% by weight. The equilibrium surface tension was measured
114 by the pendant drop method [33], and equaled to 30.7 mN/m.

115 A bubble was formed by injecting air onto a plastic cup with a diameter of 12.6 mm. Subsequently,
116 the charged Teflon surface was gradually moved closer to the bubble. If the charged Teflon surface
117 was moved too close or too fast, the bubble forms a cone shape. Subsequently, a small liquid bridge
118 was formed and detached from the bubble. The formation of a liquid bridge has been reported
119 previously under a high electrical field [34]. In our system, the formation of the cone shape,
120 detachment of small liquid bridge and bubble restoration, happened within 20 milliseconds. Such
121 dynamic behavior was only obtainable with a high-speed camera. An example of the process
122 (captured by a FASTCAM SA4 model 500K-M3) is showed in Figure 2. The image sequence
123 demonstrated the fast ion separation and movement, within milliseconds. Consequently, it is
124 expected that ionic rearrangement within the thin film reached the equilibrium quickly for non-
125 bursting conditions.





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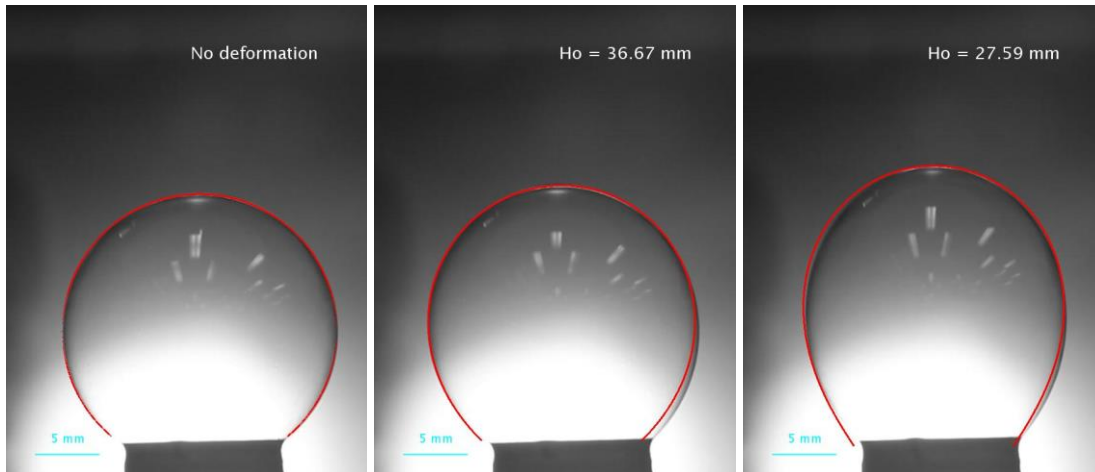
127 Figure 2. Dynamic deformation of the bubble, captured with a high-speed camera at 1000 frame-
128 per-second.

129 The minimum distance for the non-bursting condition was ~ 21 mm. Consequently, moderate
130 distances, $H_0 > 21$ mm, was employed for the model validation. The bubble shape was captured
131 using a digital camera at a resolution of 5184×3456 pixels for image analysis.

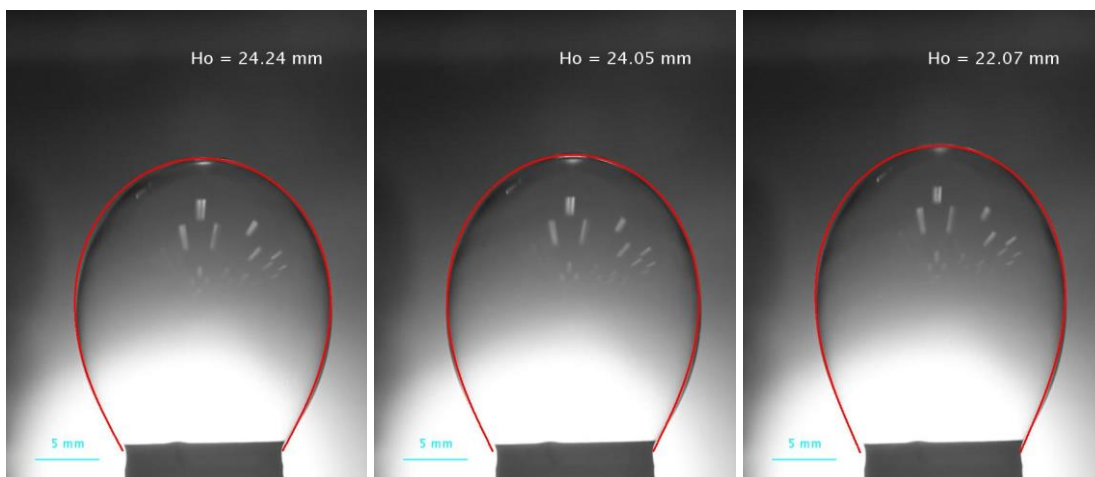
132 **Results and Discussion**

133 The bubble shapes at different distance H_0 are shown in Figure 3. It can be seen that the
134 deformation, that is vertical prolongation, increased with the decreasing H_0 . Notably, the radius of
135 curvature at the apex of the deformed bubble was smaller than the middle region. The reduced
136 principle radius indicated quantitatively that the film tension at the apex was smaller than that in
137 the middle region, which means b_l is smaller than 1.

138

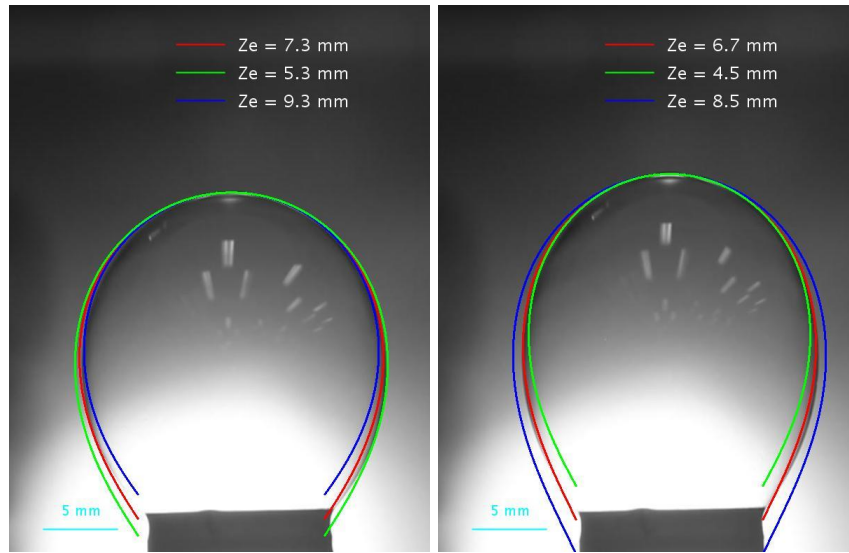


139



140 Figure 3. Bubble deformation: experimental images and modelled prediction (red curve) at
141 different H_0 .

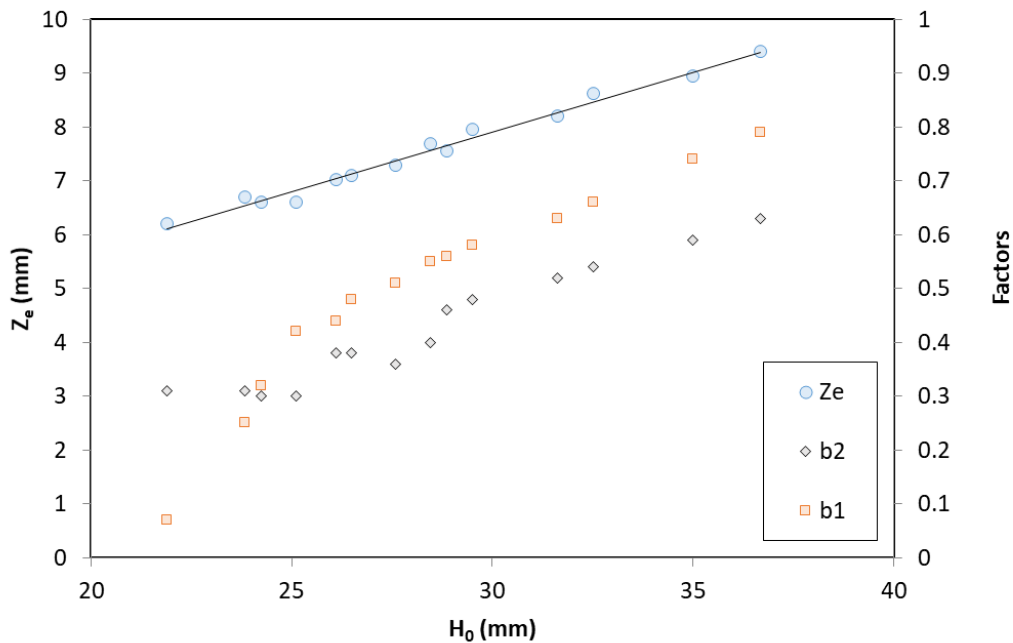
142 The modelling was applied to each bubble shape to determine out the corresponding values of the
143 three fitting parameters. In addition to the best-fitted values, the model can predict the bubble
144 shape at different values of Z_e (Figure 4).



145

146 Figure 4. Influence of Z_e on the shape of bubble: (left) $H_0=27.59$ mm and (right) $H_0=24.05$ mm
 147 (red curves are best-fitted)

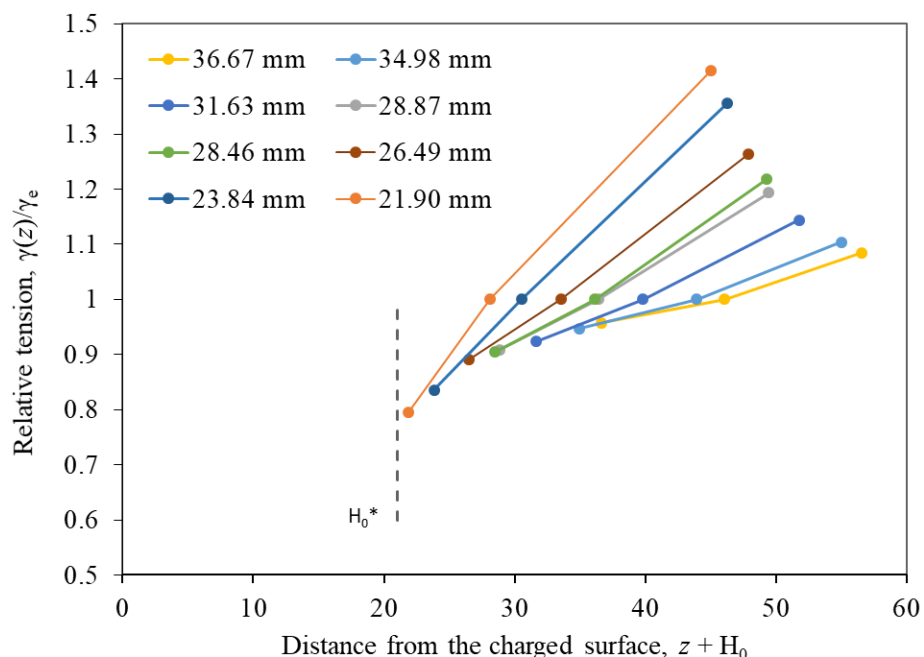
148 The best-fitting values are plotted in Figure 5 as function of H_0 . The value of Z_e follows a linear
 149 correlation with H_0 . The linearity is physically consistent with the electrostatic field: the position
 150 of neutral charge is pushed further down as the charged surface moves closer. As H_0 approaches
 151 infinite, both b_1 and b_2 approach unity as expected. As H_0 approaches the limitation of 21 mm,
 152 both b_1 and b_2 were reduced. The decreasing trends of b_1 and b_2 (between 0 and 1), indicate a
 153 higher slope of the ionic gradient. It is noteworthy that b_1 was dramatically dropped to zero as H_0
 154 ~ 21 mm. Qualitatively, the trends are consistent with the increasing strength of the electrostatic
 155 field.



156

157 Figure 5. Model parameters as functions of H_0 .

158 The model validates that the non-neutral conditions can be maintained at equilibrium. The
 159 inequality between the surfactant and its counter-ion generate the variable tension. While the local
 160 ionic gradient within the thin film is unknown, the film tension is variable with distance as plotted
 161 in Figure 6. The value of the film tension is lower at the apex, which contains fewer anions. As
 162 distance H_0 is reduced, the anion concentration at the apex is gradually reduced. Qualitatively, the
 163 trend indicates that Br^- has a positive impact on the film tension.



164

165 Figure 6. Relative tension as a function of H_0 . Each line represents the tension profile of a bubble
 166 shape (the three points along each line represent the positions of the apex, the neutral point and
 167 base of the bubble, respectively).

168 To quantify the individual impacts of anion and surfactant, a critical separating distance is
 169 considered. It has been showed that the ionic pairing of counter-ion with the adsorbed surfactant
 170 are variable with the electrostatic strength. For instance, the binding varied with the space length
 171 the cationic Gemini surfactants,[35] and the hydration shell of the anion [36]. Hence, it is expected
 172 that the anions can be completely displaced by a sufficiently strong electrostatic field.
 173 Consequently, there is a critical distance, H_0^* , at which the liquid film at the apex has no free
 174 anions. Further decrement of H_0 would break the liquid film and form a charge liquid bridge as in
 175 Figure 2. From the high-speed images and Figure 5, it can be estimated that the value of H_0^* for
 176 the studied system is ~ 21 mm. At this distance, the film tension, γ^* , at the apex is dominated by
 177 surfactant molecules solely. It should be noted that the value of H_0^* is dependent on the surfactant
 178 system and surface charge. A lower charge density or lower surfactant packing will increase the

179 distance. Teflon was one of the highest insulators. From the static voltage of -19.7 kV, the charge
 180 density of Teflon plate is calculated at 0.7×10^{-6} mol/m². Similar, CTAB is strongest cationic
 181 surfactants, with saturated adsorption $\sim 3 \times 10^{-6}$ mol/m²[37]. The critical distance is also influenced
 182 by the bubble size: a smaller bubble will have higher ΔP and smaller H_0^* . As the results, the critical
 183 distance for the studied system was sufficient small for optical observation. The slope between the
 184 apex and the neutrally charged position, $H_0^* + Z_e^*$, was highest at this distance (Figure 5). This
 185 critical gradient can be estimated at the practically obtainable distance of $H_0 = 21.9$ mm. Hence,
 186 the value of γ^*/γ_e is estimated at 79%.

187 The surface tension, or film tension, is dominated by the H-bonds of water molecules [38]. In the
 188 presence of cationic surfactants, both surfactant and hydrated anions reduce the surface tension by
 189 disrupting the interfacial H-bonds of water surface. While the alkyl tails directly disrupt the water
 190 layer [39], the hydrated anions affects the tension via the interaction of hydration shells [40–42].
 191 Quantitatively, the reduction in film tension is given by:

$$192 \quad \gamma_0 - \gamma(z) = \varepsilon_s \Gamma_s(z) + \varepsilon_a \Gamma_a(z) \quad (7)$$

193 Where γ_0 is the film tension of pure solvent (144 mN/m); ε_s and ε_a are the molecular impact of the
 194 surfactant and hydrated anion, respectively; $\Gamma_s(z)$ and $\Gamma_a(z)$ are the local adsorption concentrations
 195 of surfactant and anion, respectively.

196 Since the surfactant adsorption is governed by hydrophobic force, it can be assumed that Γ_a remains
 197 constant. At the neutrally charged position, $H_0^* + Z_e^*$, $\Gamma_a = \Gamma_s$. At H_0^* , there is no free anions at the
 198 apex. Assuming a complete ionic separation, one can expect $\Gamma_a = 0$ at the apex. Applying Eq.(7) to
 199 these two positions, the ratio between ε_s and ε_a can be determined as:

200
$$\frac{\varepsilon_a}{\varepsilon_s} = -0.14 \quad (8)$$

201 The negative sign indicated that Br⁻ has an opposite contribution to surfactant. The results are
202 consistent with a simulation study on the individual influence on the surface tension [15]. The
203 positive contribution of Br⁻ to the film tension is also consistent with the increased surface tension
204 by halide salts [43–45]. The study can be extended to anionic surfactant systems, which is
205 important for cations removal [4], with a positively charged surface.

206 **Conclusions**

207 The soap film tension gradient is experimentally observed under an electrostatic equilibrium. It
208 was revealed that the surfactant layer and counter-ions can be separated locally and have a
209 significant effect at the micro-scale. The modelling results verified some quantitative assessment
210 of the thin film. The surfactant and anion have opposite contributions to the film tension. While
211 surfactant reduces the tension, anion increases the tension. For the studied system, the impact of
212 the anion is much weaker (~14%) than that of the surfactant and thus is cancelled out.

213 It should be noted that the tension-induced surface deformation has been reported as the famous
214 “tear of wine” or Marangoni phenomena. In the instance, the variable surface tension was caused
215 by the composition gradient along the surface, which was maintained dynamically. On contrast,
216 the obtained gradient in this study was generated by a static displacement between anion and
217 surfactant. Finally, it is interesting to note that the bubble can be busted by a charged object without
218 direct contact. The method can be extended to explore the molecular structure of the interfacial
219 layer and control the foam stability. A routine software combining image analysis and numerical
220 modelling will be useful for soap film analysis. Such modelling program can be applied *in-situ* to

221 provide timely insights into the composition of foaming films, which is variable during industrial
222 processes.

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225 on Youtube (<https://www.youtube.com/watch?v=aySWX55-xX4>).

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