The effect of vessel wettability on the foamability of 'ideal' surfactants and 'real-world' beer heads.

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Abstract

The ability to tailor the foaming properties of a solution by controlling its chemical composition is highly desirable and has been the subject of extensive research driven by a range of applications. However, the control of foams by varying the wettability of the foaming vessel has been less widely reported. This work investigates the effect of the wettability of the side walls of vessels used for the *in situ* generation of foam by shaking aqueous solutions of three different types of model surfactant systems (non-ionic, anionic and cationic surfactants) along with four different beers (Guinness Original, Banks's Bitter, Bass No 1 and Harvest Pale). We found that hydrophilic vials increased the foamability only for the three model systems but increased foam stability for all foams except the model cationic system. We then compared stability of beer foams produced by shaking and pouring and demonstrated weak qualitative agreement between both foam methods. We also showed how wettability of the glass controls

bubble nucleation for beers and champagne and used this effect to control exactly where bubbles form using simple wettability patterns.

Keywords

Foamability

Foam stability

Wettability

Contact angle

Beer head control

Hydrophobic-hydrophilic

Introduction

Aqueous foams are metastable arrangements of tightly packed gas bubbles stabilized by surface-active molecules at the gas / liquid interface and have a wide range of uses from mineral extraction and firefighting to cosmetic and culinary uses. It is well known that the foamability and stability of foams can be influenced by a range of factors including the type [18] and concentration [3] of surfactant used and the foam generation method [25]. In addition, for beer, the bubble size is mainly determined by surface tension, the shape of the nucleation site and the contact angle between the liquid and the nucleation site. [19]

The vast array of foam applications has resulted in a wide range of test methods and characterization methodologies such as the general Ross-Miles [20] and Bickerman [12] tests and also more application specific tests such as the Rudin and NIBEM test in the brewing industry [1],[23].

Recent studies have shown that the size and wettability of the vessel used for foam formation can influence the foam properties: Cheah *et al.* [4] have shown that the amount of foam generated from the anionic surfactant sodium bis-2(ethylhexyl) sulfosuccinate (AOT) by the plunging jet method decreases if a larger vessel is used. Such dependence on container size has also been shown by Papara *et al.* [15] who showed in addition that the wettability of the sidewalls of the foam generation vessel is important when generating foams from a mixture of soya protein isolate and xanthan gum using a kitchen mixer. They studied foam formation in Plexiglass containers with volumes of 200mL, 600mL and 2100mL and charactersied the wettability of the walls by the contact angle θ measured between the surface of a water droplet and the solid surface. They studied foam formation in Plexiglass containers with volumes of 200mL, 600mL and 2100mL and characterised the wettability of the walls by the contact angle θ, which describes the equilibrium shape of a droplet on a surface, a balance between the cohesive and adhesive forces. In the case that the liquid 'wets' a surface, the liquid will spread to a small or even zero contact angle on the solid surface; conversely when the contact angle is large, the drop stays more or less in a spherical shape, in which case the liquid is called 'non-wetting'. Frequently when an aqueous liquid wets a surface this surface is called 'hydrophilic' and if not, the surface is called 'hydrophobic' [26].

The contact angle of the inside of the containers used by Papara *et al.* [15] was between 75° - 112°. They observed higher drainage rates in hydrophilic ($\theta \sim 75°$) vessels in but in hydrophobic ($98° < \theta < 112°$) vessels the drainage rates were found to be slightly lower. They also found that such dependence on the wettability of the vessel decreased as the vessel size increased. Zuidberg

[27] studied the effect of the wettability of a container on the head of beer by using containers made of different materials. Glass containers ((static contact angle (θ) = 0° and advancing contact angle (θ_A) = 45°) generated the most foam of the samples studies while both Perspex (θ = 45°; θ_A = 90°) and Teflon foil containers (θ = 90°; θ_A = 100°) generated very little foam and also formed large bubbles in the bulk of the liquid. These two studies appear to contradict each other, with Papara et al. [15] finding that the hydrophilic containers produced the least amount of foam while Zuidberg [27] found that the hydrophilic surfaces produced the most foam. This fact that different liquids were used as foaming agents suggests that the picture of predicting foam properties based simply on the wettability of the foam container may be difficult.

We investigated the wettability of glass vials used for *in situ* foam generation over a wider range of contact angles ($20° < \theta < 114°$) compared to previous work [15]. The purpose is to investigate the critical contact angle responsible for any difference in foam behavior as the wettability of the surface with which it is in contact decreases. We also determine the effect of the surfactant type (non-ionic, anionic and cationic surfactants) on any changes of foam behavior resulting from a change in wettability of the solid surface. We then extend our study to look at the applications of controlling the wettability of a solid surface on foam properties by studying the effect on beers and champagne.

Experimental

Chemical functionalization of glass containers

Glass vials (neutral glass, snap top, 21.25mL, T103/V4, Scientific Glass Laboratories Ltd), 1/3 pint glasses (Toughened conical beer glass, Stephensons Catering Equipment, UK) and champagne flutes (Timeless Classic Champagne Flutes, Tesco, UK) were rendered hydrophilic by immersion in 30% hydrochloric acid (Fisher Scientific, UK) for 16 hrs. The glass containers were then rinsed using copious amounts of water and dried at 80°C for 3 hrs. The resultant hydrophilic vials were then either used for the foam tests or immersed in one of three solutions for additional surface functionalization: 2 hours in a 2% solution in ethanol of 3-aminopropyltrimethoxysilane (APTMS) (97%, Sigma Aldrich (UK)) [8]; 48 hours in a 2% solution in toluene of chloromethylsilane (CTMS) [9] (≥97%, Sigma Aldrich (UK)); 30 mins in a 5% solution in water of Grangers 'Extreme Wash In Solution' (Grangers, UK) [10]. Grangers 'Extreme Wash In Solution' is based on C8 fluorochemistry and has since been discontinued with the most closely related product currently available from Grangers being 'Performance Proofer' which is based on C6 fluorochemistry. Following the treatment, the vials were rinsed three times in the respective pure solvent, and then dried at 80°C for 3hrs. The static (θ^W), advancing (θ^W_A) and receding (θ^W_R) contact angles of a water droplet on flat glass microscope slides subjected to the same chemical treatments as the vials were measured using a Krüss DSA 10 goniometer (Hamburg, Germany) and Krüss DSA software. The measured values are shown in **Table 1**.

Foaming solutions

Aqueous solutions of common anionic (18mM sodium dodecyl sulfate, **SDS**), non-ionic (0.18mM heptaethyleneglycol monododecylether, **$C_{12}E_7$**) and cationic (5mM hexadecyltrimethylammonium bromide, **CTAB**) surfactants were used for foam generation. All of the surfactants were BioXTRA grade and purchased from Sigma Aldrich (UK) and the water used was distilled tap water. The concentrations used are significantly greater than the critical micelle concentration of the surfactants which are 8.2mM (SDS [26]), 8.2 x 10^{-3} mM ($C_{12}E_7$ [7]) and 1 mM (CTAB [11]).

The beers used in this study were Guinness Original (4.2% ABV), Banks's Bitter (3.8% ABV), Bass No 1 (4.4% ABV) and Harvest Pale (4.3% ABV) purchased in 500mL bottles and champagne (Henry Dumanois Brut (50% Pinot Noir 35% Meunier and 15% Chardonnay grapes). They were used at room temperature and none of the beer bottles contained a widget.

Foam generation

In order to generate the foams, 2mL of surfactant solution or beer, which had been allowed to degas by pouring 10ml of beer into a glass vial which was the left open for 72 hrs, were shaken in the chemically modified glass vials by hand for 1 min at a rate of 200 ± 4 shakes.min^{-1}. Images of the solutions were recorded immediately before and after shaking and at 1 minute intervals up to 1hr after shaking using a CCD camera (Imaging Source (Bremen, Germany) USB CCD camera) and controlled using IC Capture software (version 2.1 by Imaging Source (Bremen, Germany)) in conjunction with an LED backlight. Three vials, of the same hydrophobicity, each containing 2mL of surfactant solution, were foamed simultaneously before imaging. This process was repeated twice more, with the foam being allowed to collapse between each repeat. Therefore, the foam data for each combination of vial hydrophobicity and surfactant is the average of nine measurements. A similar method of generating foams via hand shaking has been used previously in beer science research, for example in [13].

Bottled drinks (beer or champagne) were poured into unmodified or chemically modified 1/3 pint glasses or champagne flutes respectively. The drinks were poured with the glass held at an angle of ~35° with the opening of the drinks bottle a distance of ~5 cm from the inside wall of the glass.

Foam characterization

Foamability is calculated as the volume of foam generated immediately after shaking (V_i), divided by the initial volume of surfactant solution (V_s), expressed as a percentage:

$$Foamability\ (\%) = \left(\frac{V_i}{V_s}\right) \times\ 100 \qquad \text{Equation (1)}$$

The foam stability is defined as the percentage of foam head remaining after 1 hour (V_f) compared to that immediately after shaking:

$$Foam\ stability\ (\%) = \left(\frac{V_f}{V_i}\right) \times\ 100\ \text{Equation (2)}$$

The foam volumes were measured using the area of the foam visible on the images, using the freely available image processing software ImageJ (http://imagej.nih.gov/ij/). It should be noted that our analysis is simple to implement and can be applied *in situ* with no specialist equipment. However it is based solely on the extent of the foam and does not take into account bubble size distributions, water content (as is often measured using resistivity) or any more sophisticated methods of characterizing foam density or structure.

Results and Discussion

Model surfactant systems

Figures 1 and 2 show qualitatively in images and quantitatively how the wettability of the inner surfaces of the vial used to generate the foam affected both the foamability and foam stability for the three model surfactants. **Figures 1a-c** show the foamability of the model surfactant solutions were unchanged for θ^W of the glass vials at or below 79.4° (CTMS modified vials) but decreased significantly when θ^W was increased to 113.5° (Glass modified with Granger's solution). The graphs in **Figure 2** support these observations as the foamability for all three model surfactants dramatically decreased from around 300% in hydrophilic vials to approximately 100% in hydrophobic vessels, with the transition occurring with a contact angle somewhere between 79.4° and 113.5°. We arbitrarily choose the transition contact angle to be 90° as this contact angle represents the boundary between hydrophobic and hydrophilic behaviour of solid surfaces.

This observation is in agreement with Papara *et al.* [15], who demonstrated a difference in foam properties between hydrophilic and hydrophobic Plexiglass containers. Such a general trend was not observed for foam stability, however, which appeared to depend on the nature of the surfactant. While the stability of CTAB (cationic) foam was around 75% irrespective of vial wettability, the stability of foams made from $C_{12}E_7$ (non-ionic) decreased slightly (34% to 20%) and SDS (anionic) exhibited a greater reduction (45% to 15%) in hydrophobic vials. Wagner et.al. [24] reported that CTAB could be used to shield water from the hydrophobic nature of soils in order to increase the water uptake. A similar mechanism may be present in the system that we studied which may have acted as to preserve the stability of CTAB foams. Petvoka et.al. [17] also compared the foamability and stability of three model surfactants SDS, C_{12}TAB (as opposed to our C_{16}TAB) and a different non-ionic surfactant Brij 35, at lower overall concentrations than here, and in the presence of 10mM NaCl. Despite these differences, they also found little variation in foamability between the different surfactants, with values around 130% at 1mM concentration. As their foams were only stable for several minutes, it is difficult to directly compare the stability measurements. However, in direct contrast to our results, they did find that their cationic foam (C_{12}TAB) was significantly less stable than both their anionic and non-ionic foams. This suggests that simply classifying foams by the ionic nature of the surfactant is not sufficient to predict foam behavior, and more in depth information regarding the specific molecule is required.

We also performed similar experiments using 2mL of beer (Guinness Original, Banks's Bitter, Bass No 1 and Harvest Pale) in vials that were either hydrophilic (HCl cleaned) or hydrophobic (HCl cleaned and then modified with Grangers solution). **Table 2** confirms that glass microscope slides cleaned in HCl exhibit beer contact angles (θ^B) less than 90° and those Grangers' modified microscope slides display contact angles greater than 90° so the vials can be considered 'beerophilic' and 'beerophobic' respectively. The necessity to check the beer contact angles is that the surface tension of beer is less than water as is shown by the beer contact angles (**Table 2**) being less than the ones of water droplets on equivalent surfaces (**Table 1**).

The vial shake tests of these beers suggested that it was the foam stability, rather than foamability, that was most affected by the hydrophobicity of the glass surface (**Figure 3**). Such an observation suggests that beer foams behave differently compared to aqueous solutions of 'model' surfactants but the wettability of the glass container does have a noticeable effect on the foam properties. This is unsurprising given that beers are far from 'model' surfactants as the foams are stabilized by complex proteins from the malt [5].

Figure 4 summarises the change of foam properties between hydrophobic and hydrophilic vessels: the horizontal axis is the change in foam stability and the vertical axis the change in foamability. All beers exhibited approximately zero change in foamability, in rank order Guinness showing a slight increase, Bank's Bitter and Bass No.1 a similar small decrease and Harvest Pale a larger decrease. They all showed a comparable increase in stability of around 25% (range: 20 – 29%). In contrast, all model surfactants were found to have a much larger increase in foamability of around 175% (range: 131% - 244%) but the change in stability is dependent on the surfactant charge. This indicates that characterisation by contact angle alone is not sufficient to capture the full complexity of the behaviour and the nature of the specific interactions between molecules in the solution and the surface must be taken into account. It would be interesting in future work to investigate an extended range of model surfactants, to extract particular foam positive and negative constituents from beer [1, 2] and to fully characterize the surfaces. **Figure 4** represents the first step towards a phase diagram to show how different foam stabilizers behave on hydrophobic and hydrophilic surfaces and may lead to better understanding of the liquid-solid-air-interactions in these foaming systems.

Beer and Champagne pouring tests

The same beers that were studied in the 'vial shaking tests' were poured into chemically modified glasses in order to compare the effect of the wettability of the glass on the beer head. As can be seen in **Figure 5** the wettability of the beer glass had an influence on the formation of the beer foam heads. The size difference of the initial foam head (foamability) between the beer poured into hydrophilic and hydrophobic glasses was greatest for Guinness Original and less for both Banks's Bitter and Bass No 1. The effect of the wettability of the glass appeared to have little effect on the small foam head generated from the Harvest Pale. In rank order, this is the same as was found for the shaking tests, although it is difficult to compare the two methods quantitatively. The stability of the beer heads decreased significantly in the hydrophobic glasses compared to the hydrophilic glasses apart from the Harvest Pale that was not affected greatly by the wettability of the glass as is shown in **Figure 5**, however the head was so small it is hard to draw meaningful conclusions. The graph in **Figure 6** shows numerically that the head height and the stability increased for Guinness, Bank's Bitter and Bass No 1 in the hydrophilic glasses, whereas Harvest Pale shows a reduction in both.

For all beers, the bubbles on the inside of the hydrophobic glasses were significantly larger, and much less mobile, than those observed on the inside of the glasses that were rendered hydrophilic. This observation, consistent with previous work [27], is presumably from the dewetting processes occurring at the liquid-solid interface in the hydrophobic glasses. Bubbles preferably nucleate at defects and are more prevalent on hydrophobic surfaces compared to hydrophilic surfaces [14] on which the liquid will wet the solid surface and could act to prevent bubble nucleation by filling nucleation sites. [1]

The observation of large, relatively immobile bubbles on the inside of hydrophobic glasses were also observed with champagne (**Figure 5**). It is known that champagne bubbles nucleate at hollow fibers on the interior wall of the glass [14]. The observation that champagne bubble formation is significantly different in hydrophobic glasses compared to the hydrophilic glasses suggests that hydrophobic surfaces being able to successfully trap a small gas phase in a gas saturated liquid [17,[22]].

Patterned bubbling is currently achieved in drinks glasses by etching the glass so that the bubbles in the drink amplify the pattern etched into the glass [2] [6] [16]. Creating patterning of differing wettability on the inside of a glass would allow 'hydrophobic control' of foaming and has the potential to either compliment or replace such etched patterns with a patterning method which is invisible to the naked eye. The potential of such patterning is shown in **Figure 7** where Guinness was been poured into a glass that had one half of it hydrophobized and this resulted in a clear distinction between the two halves of the glass that exhibit differing wettability.

Conclusions

We have studied the foaming properties of aqueous solutions of common anionic, non-ionic and cationic surfactants foamed in glass vials of different wettability and found that highly hydrophobic vials ($\theta > 90°$) suppress the foam formation which is in agreement with previous findings in the literature [4],[15],[27], where different methods of foam generation were used. We also showed that this effect is independent of surfactant type when considering anionic, cationic and non-ionic systems. However, the surfactant type seems to be important when considering foam stability as the stability of anionic surfactant (SDS) foam was influenced by hydrophobic surfaces to a much greater extent than the cationic (CTAB) and non-ionic ($C_{12}E_7$) species studied.

We also investigated whether our findings could be applied to beer glasses by looking at the effect of the wettability of the containers on the foam properties of four different beers. We started by using the ‘vial shake tests’ to directly compare the beers to the model surfactants and then furthered our investigated by conducting pour tests of the beer into chemically modified beer glasses. The hydrophobic glasses into which the beers were poured suppressed both the formation of the beer head and the stability of the bubbles for all beers apart from the Harvest Pale. This suggests that the difference of the beers, possibly the different proteins present in the beer, can lead to differing foaming behavior that can be difficult to predict, but appears to be consistent between shaking and pouring methods. Future work should investigate a wider range of model surfactants, fully characterized surfaces and an attempt to isolate the important foaming components in beer. Additionally, the effect of gas solubility should be investigated, as it is well known to play an important role in foam stability. Some beers, for example Guinness, are saturated with nitrogen, which is less soluble than CO2 and therefore helps stabilize the foam. It would be interesting to compare the relative effects of surface wettability and gas solubulity. The impact of the retention of the flavor of the beer, along with the stability of the chemical modification of the glass, will also need to be the subject of future research. Findings may be important for other applications, where foam formation can be a problem such as the bottling of fruit juices.

Finally, using patterned chemical modification to vary hydrophobicity across a single surface, the location of bubble nucleation may be controlled without the need for etching. This approach could be adopted by the beer industry so that a pattern in the glass only becomes visible once the drink is poured in.

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Figures

Figure 1. Montages showing the foaming behaviour of aqueous solutions of a) sodium dodecyl sulfate (SDS; 18mM), b) heptaethyleneglycol monododecylether ($C_{12}E_7$; 0.18 mM) and c) hexadecyltrimethylammonium bromide (CTAB; 5 mM) foamed in situ in chemically modified glass vials displaying four different wettabilities (shown on the left hand side of the figure alongside their static water contact angle (i) HCl, (ii) APTMS, (iii) CTMS, and (iv) Grangers).

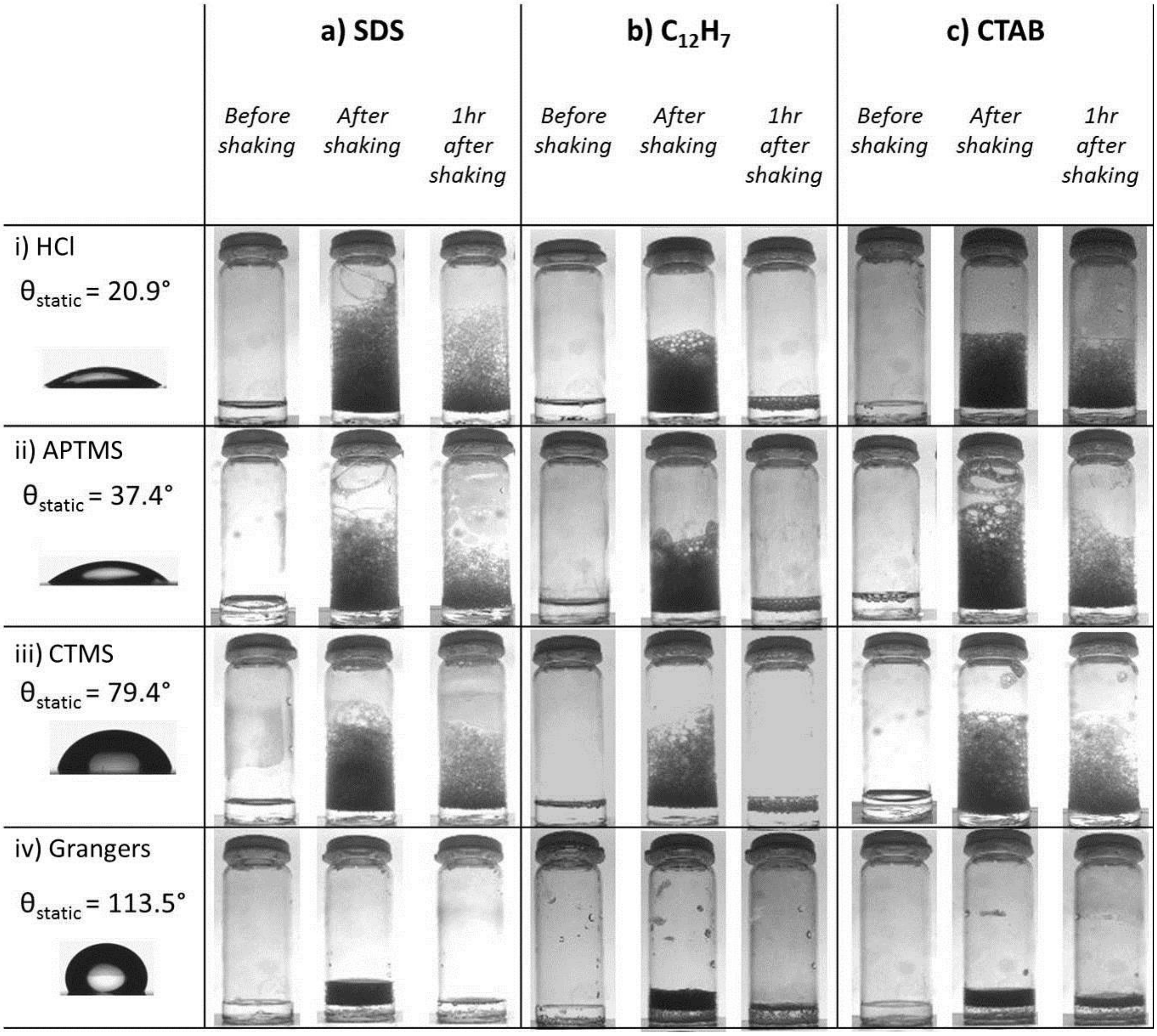

Figure 2. Graph showing the foamability vs foam stability of three 'model' surfactant systems. The foams were generated by shaking the vials by hand. Open symbols represent vials with water contact angle θ <90° and filled symbols represent vials with θ > 90°.

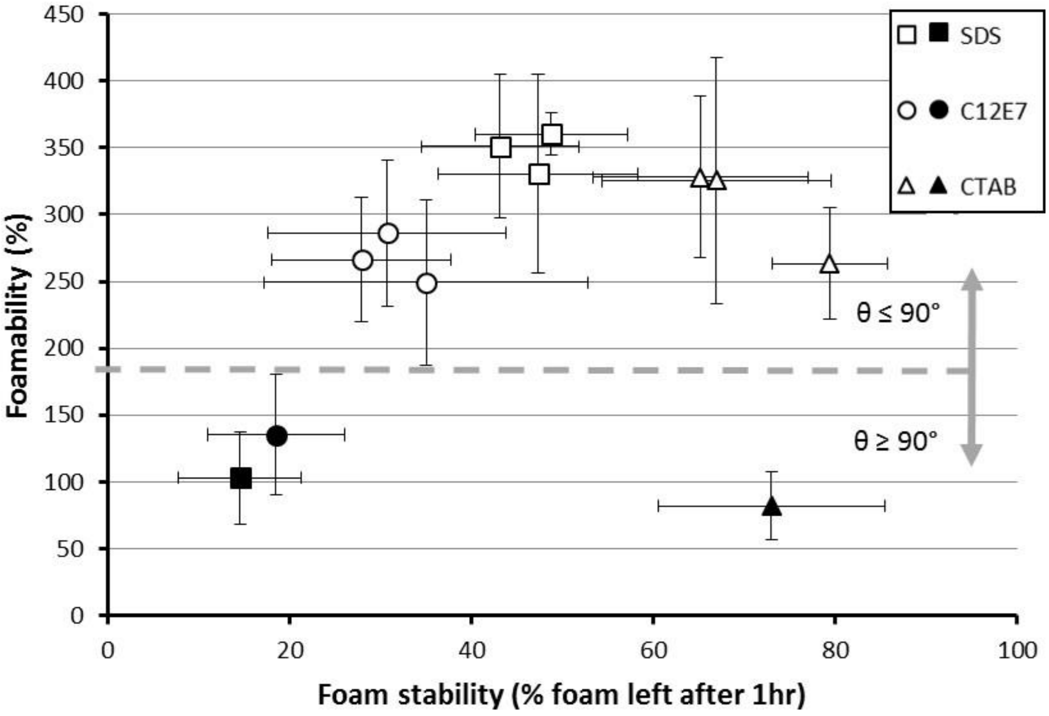

Figure 3. Foamability v foam stability graphs for foam generated from four different beers by shaking 2mL of each beer in hydrophilic (open symbols) and hydrophobic (filled symbols) vials

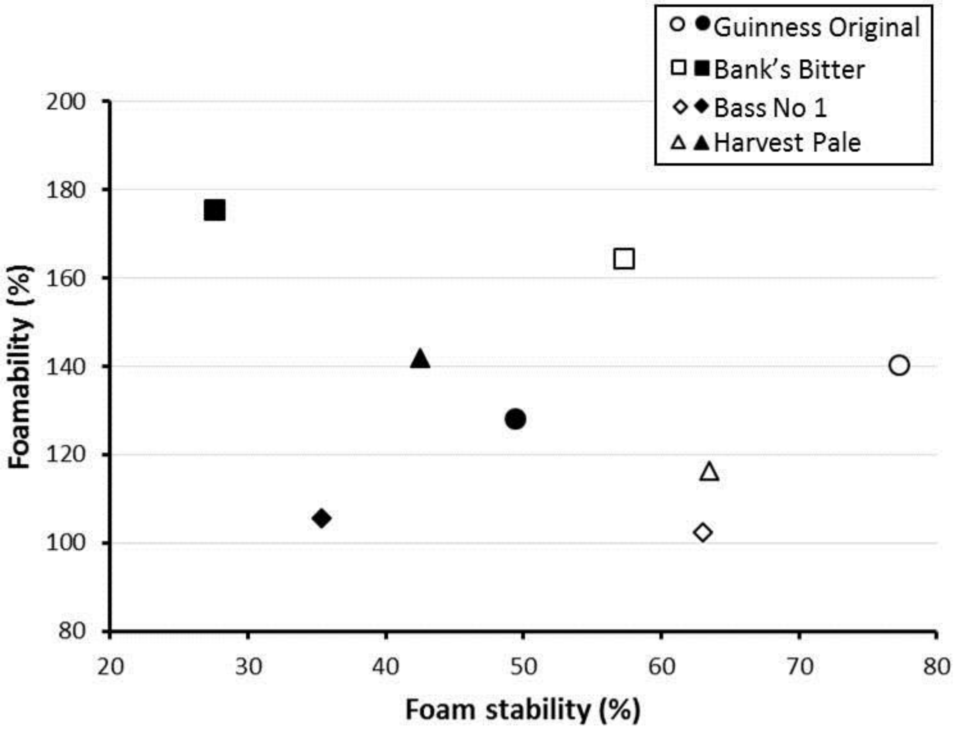

Figure 4. Graph showing the difference in foam properties between foams generated in hydrophobic and hydrophilic vials from various ‘model’ aqueous surfactant solutions and beers.

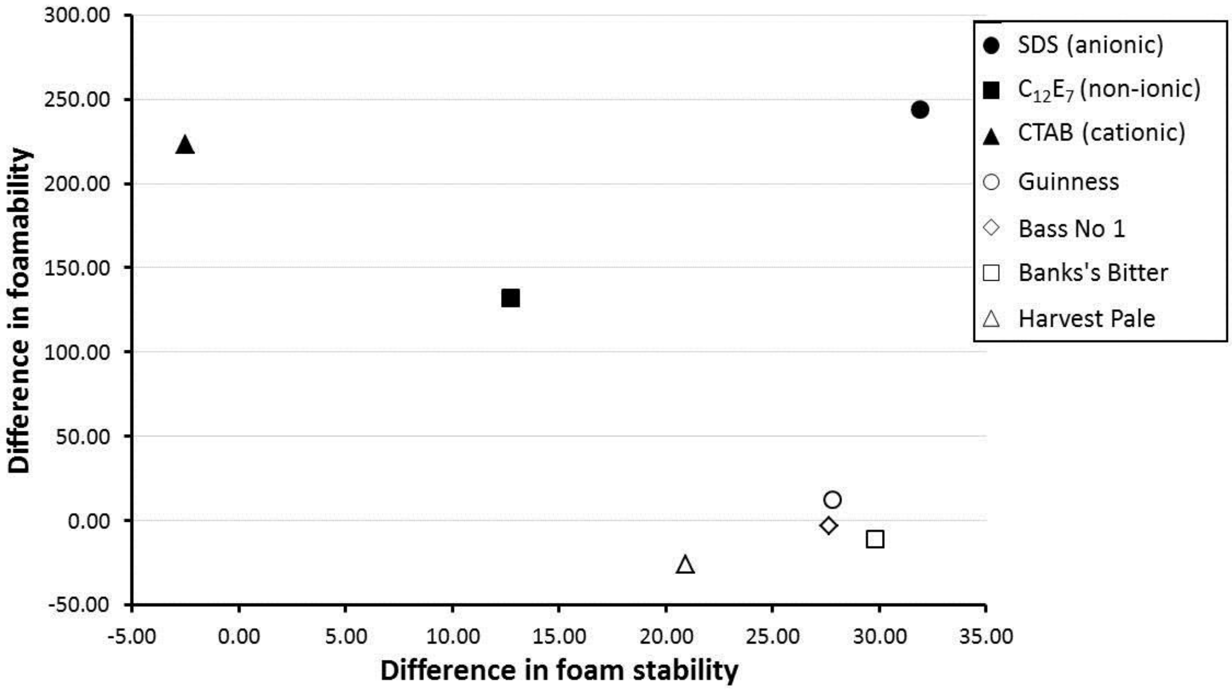

Figure 5. Images showing the effect of hydrophilic and hydrophobic glasses on the foaming properties of four different beers after being poured from their bottle by hand. The scale bars for the beer images are 20mm for the images in which both glasses are shown and 5mm for the images of only the foam head.

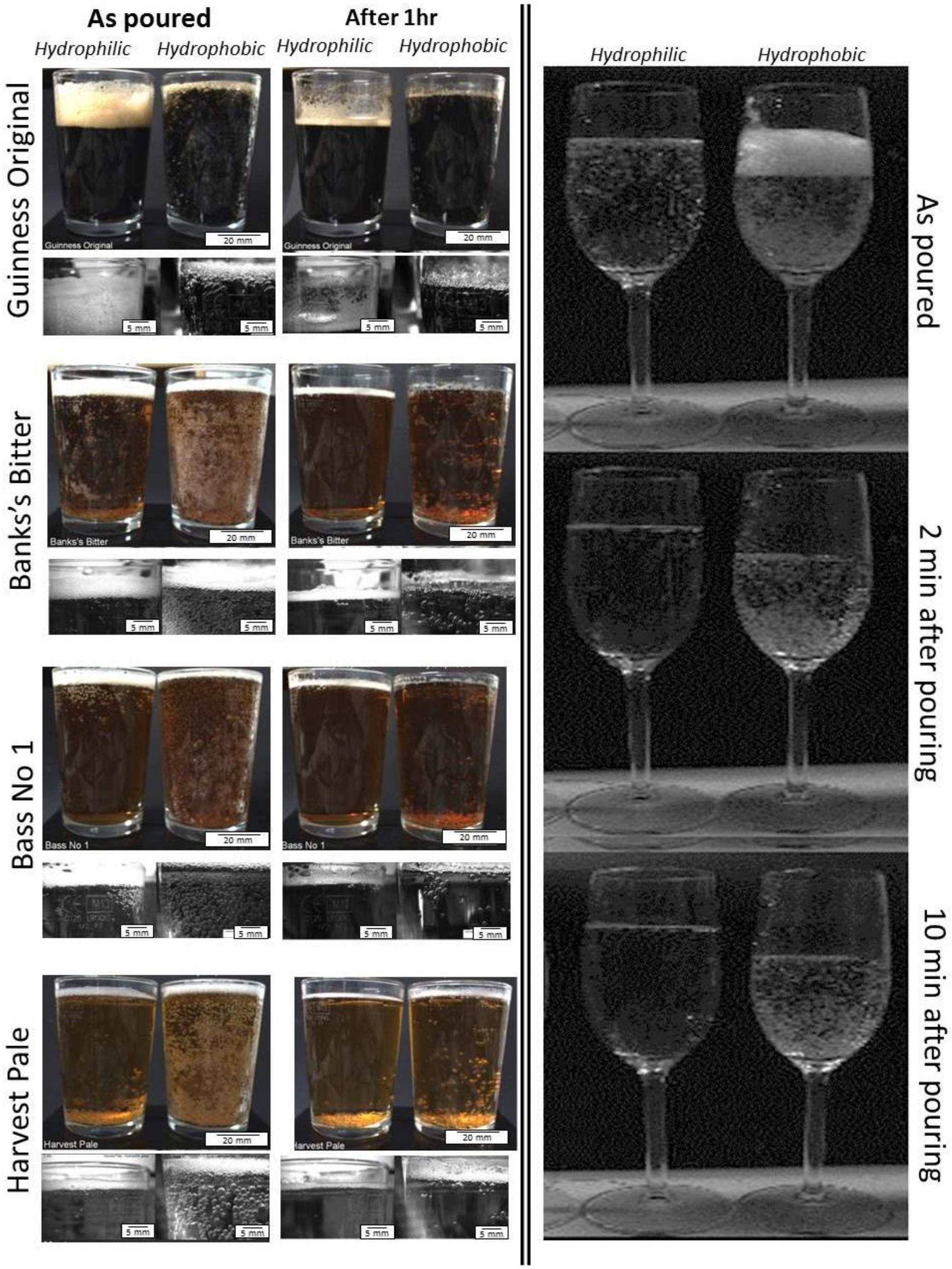

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Figure 6. Stability and height of foam head formed from hand pouring different beers into hydrophilic (open symbols) and hydrophobic (filled symbols) glasses

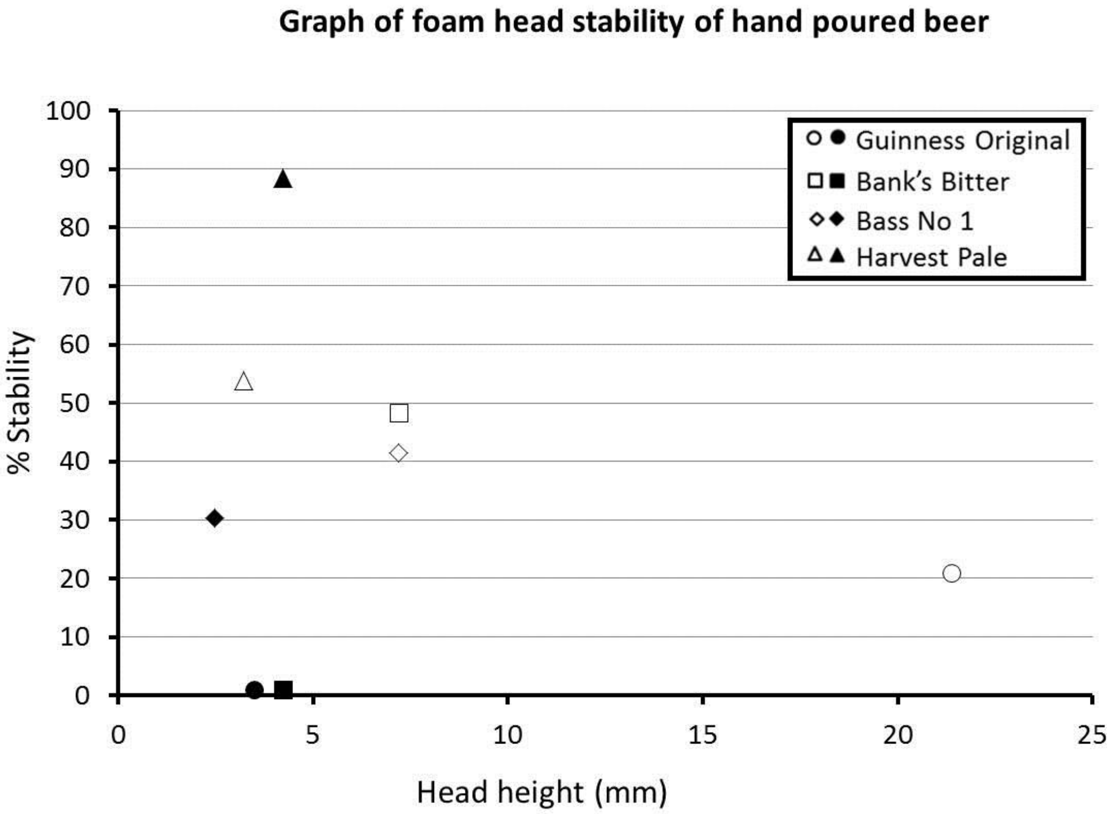
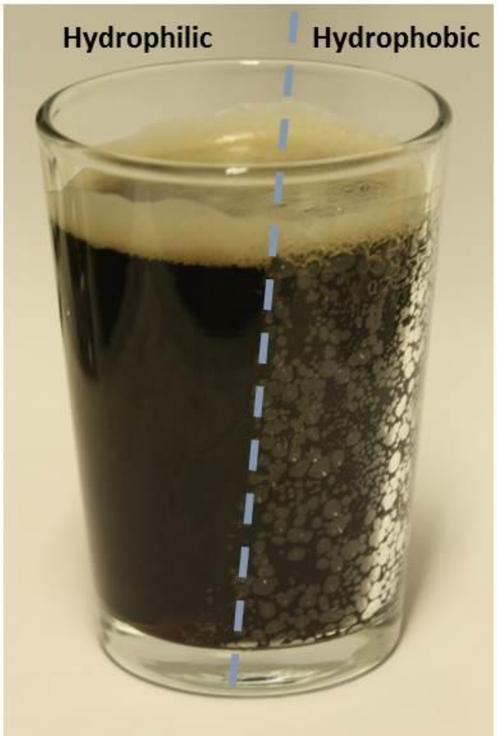


Figure 7. Guinness after being poured into a glass that had been half submerged in Granger's solution



Tables

Table 1. Water **c**ontact angle data of glass microscope slides treated in the same way as the glass vials for foam generation

	HCl cleaned	HCl cleaned then immersed in APTMS	HCl cleaned then immersed in CTMS	HCl cleaned then immersed in Grangers
Static contact angle (θ^W)	20.9° ± 3.0°	37.4° ± 4.2°	79.4° ± 1.4°	113.5° ± 1.0°
Advancing contact angle (θ^W_A)	25.8° ± 3.3°	47.9° ± 4.0°	89.8° ± 1.8°	115.6° ± 2.8°
Receding contact angle (θ^W_R)	0° (pinned contact line)	19.1° ± 5.8°	74.5° ± 1.2°	100.3° ± 3.5°

Table 2. Contact angle of different beers on hydrophilic (HCl washed) and hydrophobic (modified with Grangers) glass slides

	Guinness Original		Bass No 1		Banks's Bitter		Harvest Pale	
Vial Treatment	HCl	Grangers	HCl	Grangers	HCl	Grangers	HCl	Grangers
Static contact angle (θ^B)	28.5° ±2.0°	109.2° ±1.2°	21.5° ±4.8°	99.6° ±2.0°	19.0° ±4.5°	105.2° ±2.5°	30.1° ±2.6°	103.6° ±1.4°
Advancing contact angle (θ^B_A)	22.3° ±2.1°	115.3° ±1.1°	22.6° ±2.5°	108.3° ±2.5°	23.1° ±4.2°	111.2° ±2.9°	30.9° ±2.8°	109.6° ±1.6°
Receding contact angle (θ^B_R)	4.2° ±2.4°	15.8° ±2.6°	4.1° ±0.6°	9.6° ±2.0°	6.2° ±1.3°	19.9° ±1.4°	6.3° ±0.8°	13.3° ±3.7°