The Relative Significance of Physics and Chemistry for Beer Foam Excellence: Theory and Practice

C.W. Bamforth[1,2]

ABSTRACT

J. Inst. Brew. 110(4), 259–266, 2004

Bubble nucleation sites in beer glasses should be uniformly small to ensure that the foam produced comprises homogenously small bubbles with attendant reduced degrees of disproportionation. The latter phenomenon is also hindered by increased film thickness in foam, which in turn will be enhanced by increased localised viscosity, encouraged perhaps by polysaccharide-polypeptide complexes. Erring on the "high end" of specification for carbon dioxide will promote replenishment of foam through beading. Nitrogen at a relatively low level (15–20 ppm) will hinder disproportionation with limited suppression of hop aroma and introduction of undesirable textural features. Hydrolysed hordein appears selectively to enter beer foams at the expense of the more foam-stabilising albuminous polypeptides, suggesting that any future procedures that might selectively eliminate hydrolysed hordein components from beer would be expected not only to enhance haze stability but also foam, by eliminating species that preferentially enter into the bubble but have less foam-stabilizing capability once they are there.

Key words: Foam, physics, polypeptide.

INTRODUCTION

Over half a century of research has been devoted to the understanding of beer foam, the vast majority of which having been targeted on gaining an appreciation of the relationship between the chemical composition of beer and the stability of the foam that can be generated from it. However as previously pointed out by this author[1], "*in the various studies of foaming polypeptides not a single researcher has reported a dramatic impact on foam if the level of those polypeptides was changed. . . . Efforts to enhance beer foam by boosting the levels of foaming polypeptide from exogenous sources have highlighted the fact that most beers contain ample endogenous foaming power . . . any Brewer who has experimented with nitrogen gas, widgets or, indeed, dispense tap geometry, cannot fail to have noted the remarkable foaming potential available from any lipid-free beer.*"

The question is begged concerning which is the more important: the physical events that are involved in foam formation, retention and adhesion (lacing, cling), or the chemical composition of the beer. There is no question that they are mutually interactive, for instance one cannot generate stable foam unless surfactant materials are present. However can we achieve excellent foams from relatively modest levels of surfactants by attention to physical parameters? [In passing it must be mentioned that unquestionably the presence of any lipid or detergent materials in beer or the containers to which beer is introduced is overwhelmingly detrimental to foam. This issue is not the central focus of the present paper.]

I seek to step back from the customary manner by which a biochemist approaches the foam conundrum. Rather I wish to proceed methodically and intuitively through the physics of foaming, overlaying it with the recent observations from this laboratory concerning the chemistry. I seek to illustrate the significance of all the physical and chemical parameters by inserting "real-life" numbers into the formulae and equations that have been generated to explain foaming phenomena, thereby illustrating the relative impact that the variable parameters measurable in beer are likely to have on foaming.

THE PHYSICS OF BEER FOAMS

The doyen of foam physics is Dr Albert Prins of Wageningen. The reader is advised to search out his articles (e.g. [18,19]) and also that of Walstra[22] for a detailed, if challenging to the non-specialist, description of the various physical events in foaming.

Seeking to simplify the somewhat complex math involved, we can reduce the key events involved in foam formation and retention to the following:

- Bubble formation
- Creaming (bubble rise)
- Disproportionation
- Drainage

They are not independent events. Thus, for instance, the extent of drainage will impact on the tendency for disproportionation to occur (the latter phenomenon being the passage of gas from a small bubble to an adjacent larger

[1] Department of Food Science & Technology, University of California, Davis, CA 95616-8598, USA.
[2] Corresponding author. E-mail: cwbamforth@ucdavis.edu

Based on a presentation made to the World Brewing Congress, San Diego, CA, July 2004.

Publication no. G-2004-1306-269

one, ultimately resulting in the collapse of the former and the growth to unattractive dimensions of the latter).

Many authors refer to coalescence (the merging of two bubbles through the rupture of the film between them), however Ronteltap[20] demonstrated that this does not contribute to the collapse of beer foam under normal conditions.

It is well established that foams comprised uniformly of small bubbles are more stable and more appealing. This being the case, it should be appreciated that a critical stage for the aesthetic appeal but also longevity of foam is the initial formation of the bubble.

Bubble formation

Although beers are supersaturated solutions of carbon dioxide, bubbles do not nucleate spontaneously[19]. A nucleation site must be present, which may be a particle, scratch on the glass or a pre-formed micro bubble. The factors governing the size of bubble that is generated are given by the equation

$$\text{Bubble radius} = [3R_m\gamma/2\rho g]^{1/3}$$

Where

R_m = radius of nucleation site (m)

γ = surface tension (mN m^{-1})

ρ = relative density of the beer (kg m^{-3})

g = acceleration due to gravity (9.8 m s^{-2})

To illustrate the impact of the equation, let us say that the surface tension of the beer is 40 mN m^{-1} and that its specific gravity is 1.01. Then if the nucleation site (e.g. a slight scratch in the glass) has a radius of 0.1 mm, then the bubble developed will have a radius of 0.85 mm. If the nucleation site has a radius one tenth of the size (0.01 mm), then the bubble developed will have a radius of 0.4 mm. To achieve the smallest possible bubble, it is necessary to have the smallest possible nucleation site. Ronteltap[20] observed that foam newly generated by bubbling gas into beer through a sintered glass filter indeed featured bubbles of radii ranging up to 0.85 mm in radius, but the average radius was approximately 0.1 mm. This implies that the sites responsible for nucleation in that instance were indeed extremely small.

Surprisingly there is little published information on the surface tension of beers. However in a study from this laboratory we measured a range of 42.8 to 47.0 in commercial products[15]. Feeding these extremes into the above calculation then we can see that, for the 0.1 mm nucleation site, the bubble diameter emerging will be 0.87 mm and 0.89 mm at the two extremes of surface tension. For the smaller nucleation site the bubbles will be 0.4 and 0.41 mm respectively. It will be seen that the surface tension makes a much smaller contribution than does the difference in nucleation site diameter.

If the reader inserts values for the diversity of specific gravities to be found in beer (say 1.000 to 1.020), they will find that this is a parameter with even less impact on bubble size when compared with the nucleation site radius.

In summary it is apparent that a brewer seeking to achieve the ideal bubble size portfolio should be focusing on nucleation opportunities that involve the lowest possible diameter sites.

Creaming

Creaming, often termed "beading", is important as an appealing spectacle in beer, but also because it replenishes the foam if it is sustained through the time for which the beer is in the customer's glass.

The frequency of bubble release and rise in beer was studied[15]. Two models were generated. The first (equation 1) was generated on the basis of measurements made with a range of beers and a single defined nucleation site (a unique glass bead). The second (equation 2) was developed under experimental circumstances where the level of carbon dioxide was standardized and, furthermore, the range of values for surface tension and density were extended by dilution of the beers with water or by the addition of ethanol. This overcomes concerns that were introduced into model 1 by a single low alcohol beer, the significance of which was fully explained in the original paper.

$$a_n^0 = 3.11C + 0.0962\gamma - 218\rho + 216 \quad (1)$$

$$a_n^0 = -10.7\gamma + 3060\rho - 2406 \quad (2)$$

Where

a_n^0 = initial nucleation activity

γ = surface tension

ρ = density

C = carbon dioxide content (vol CO_2/vol beer)

From equation 1 it is evident that it is the content of CO_2 per se which has the single most important effect on nucleation and creaming in situations where the nucleation site is defined. Let us consider a beer of surface tension 42.8 and specific gravity 1.01. Say that its tolerable CO_2 range is quoted as 2.5 to 2.7 volumes. Then at the lower figure the nucleation activity (in model 1 it was a visual interpretation on a relative scale of 0–12) is 7.71, but at the top end of specification the figure is 8.33.

Using the second model, in which nucleation activity was actually on the basis of bubble count, then if the surface tension of a beer (specific gravity 1.01) varied as much as by 3 mN m^{-1} (which is exaggerated in the extreme) then the difference in bubbles counted would be a decrease of some 15% at the higher surface tension. An increase in specific gravity of 0.001 at a fixed surface tension would be predicted to afford an increase in bubble release of less than 2%.

In the earlier work[15] the important phenomenon was deemed to be the extent to which bubbles were released and rose in the beer, not the speed at which the bubbles rose. The latter is given by Stokes' equation

$$v = \frac{2g\rho r^2}{9\eta}$$

where

v = rising velocity (m s^{-1})

g = acceleration due to gravity

ρ = mass density of the beer

r = radius of the bubble

η = viscosity of the beer (Pa s)

Clearly the extent to which the specific gravity and viscosity of beer vary within batches of one beer or between beers is unlikely to have any significant effect on the rate of bubble rise, which will tend to be of the order of 0.1–0.5 cm s^{-1}.

Drainage

As soon as foam is formed liquid starts to drain from it. The phenomenon is not simple in a medium such as beer, for example interactions occur between surfactants as a liquid film thins and thus salient parameters such as localized viscosity will change with respect to time. However let us use the simple formula customarily used to explain liquid drainage from foams[22]:

$$Q = \frac{2\rho g q \delta}{3\eta}$$

where

Q = flow rate (m^3 s^{-1})

η = viscosity of film liquid

ρ = density

q = length of Plateau border (m)

g = acceleration due to gravity

δ = thickness of film (m)

From this we can calculate that the time taken to achieve a certain film thickness, $t(\delta)$, will be given by

$$t(\delta) = \frac{6\eta h}{\rho g \delta^2}$$

where

h = height of film (m)

We can compute that an increase in viscosity of a beer from, say, 0.0016 to 0.0018 Pa·s will mean a 12% increase in the time taken to reach a given film thickness. Viscosity is comfortably the most significant factor for drainage – with surface viscosity as opposed to bulk viscosity being most relevant.

Disproportionation

It was shown[20] that coalescence (fusion) of bubbles has limited importance for beer foam stability but disproportionation (also known as Ostwald Ripening) is substantially more significant.

This phenomenon is governed by the De Vries equation:

$$r_t^2 = r_0^2 - \frac{4RTDS\gamma t}{P\theta}$$

where

r_t = the bubble radius at time t

r_0 = bubble radius at the start

R = the gas constant (8.3 J K^{-1} mol^{-1})

T = absolute temperature (°K)

D = the gas diffusion coefficient (m^2 s^{-1})

S = the solubility of the gas (mol m^{-3} Pa^{-1})

γ = the surface tension

t = time (s)

P = pressure

θ = the film thickness between bubbles

Based on inputting variables into the De Vries equation (at atmospheric pressure), Table I illustrates how the radius of a 0.5 mm bubble changes over time with a film thickness of 100 µm (a somewhat wet foam) and at different temperatures and gas compositions.

The enormous benefit to foam stability of nitrogen gas is readily apparent, as is the somewhat smaller impact of reduced temperature. For comparison purposes, if the film thickness was only 10 µm (a very dry foam), then for the case of CO_2 and 5°C, the radius of the bubble would be 0.41 mm after 10 seconds, 0.29 mm after 20 seconds and 0.02 mm after 30 seconds.

Clearly the most significant factors to protect against bubble collapse through disproportionation are gas content and the film thickness. The latter, in turn, will be impacted primarily by drainage rates (see earlier) but also by any surface active materials which enter into the bubble wall and which interact to achieve a framework capable of maintaining film integrity.

Foaming is in conflict with surface tension

The production of foam is in direct opposition to the force of surface tension. The surface tension of pure water is 73 mN m^{-1}. It is only if surface active species are present that this can be countered, such molecules going into the surface and "holding" it together. The surface tension of beers tends to be in the range 42 to 48 mN m^{-1} and in bulk is largely lowered by ethanol. Locally (i.e. in the bubble wall) it is lowered by surfactants.

To illustrate the increase in surface area: if a bubble (assuming it to be a perfect sphere) has a radius of 0.4 mm, then its volume is 0.27 mm^3, or 0.00027 mL. And so for every mL of foam there are approximately 3,700 bubbles (assuming perfect packing). The surface area of one bubble of radius 0.4 mm is 2.01 mm^2. Thus 3,700 bubbles represent a total surface area of some 74 cm^2. If the foam on a pint of beer amounts to a conservative 20 mL, then we have a foam surface area approaching 1,500 cm^2. It must

Table I. The size attained by a bubble (r = 0.5 mm; film thickness 100 µm) after different time periods in the presence of either carbon dioxide or nitrogen and at different temperatures.

Seconds	CO_2/5°C	CO_2/25°C	N_2/5°C
10	0.49	0.49	0.5
20	0.48	0.48	0.5
30	0.47	0.46	0.5
60	0.44	0.44	0.5
180	0.32	0.3	0.5
240	0.23	0.19	0.5
300	0.03	—	0.49
600	—	—	0.49

be stressed that this area rises dramatically if we consider foams comprising smaller bubbles. Thus if we substitute 0.2 mm for 0.4 mm as the bubble radius the surface area increases ten-fold.

THE CHEMISTRY OF BEER FOAMS

Foam stabilizing substances in beer

For a protein to be an effective surfactant[9,10] it must

- be able to enter the bubble wall
- be able to change once in the bubble wall, which may comprise unfolding so as to present the most effective configuration, interact with other molecules (for example, iso-α-acids) and be mobile (fluid) such that it can flow to rectify thinning in other places on the bubble surface

It has long been established that the primary foam backbone material in beer is proteinaceous. For a protein to have good foamability it must be capable of rapid adsorption and unfolding at the surface. In order to offer good foam stability, the protein must form a strong, flexible and cohesive film in order to reduce gas permeability and to inhibit coalescence and disproportionation. A single protein may not necessarily combine both attributes. Proteins with good foamability tend to be flexible, amphipathic and relatively small. This means that they diffuse rapidly to the gas-liquid interface, display strong adsorption and rapidly lower interfacial tension. Proteins displaying good foam stability form an adsorbed film that is resistant to mechanical deformation, can pack densely and are able to cross-link and aggregate. Foam stability tends to be highest at their isoelectric point. Because they display no net charge there is minimum electrostatic repulsion and hydration.

If a mixture of proteins is present, which is the case for beer of course, then the situation becomes complicated. Simplifying the case to a hypothetical one of two proteins, then if one of them is much more foamable then it will tend to "squeeze out" the one that is less foamable but which is perhaps the more foam-stabilizing. The converse situation can occur, whereby proteins interact with a net enhancement of foam stability[8,16].

How much protein is needed?

Let us consider that we have a bubble of radius 0.4 mm. Its surface area is 2.01 mm^2. Let us say that the surface area of a beer polypeptide is of the order of 50 nm^2 as it orientates itself in the bubble wall. On this basis there would be room to fit 4×10^{10} polypeptide molecules as a monomolecular layer in the bubble wall if they were capable of perfect interlocking (c.f. the panels on a soccer ball). This is a very simplistic assumption, but suitable for illustrative purposes.

Now one mole of polypeptide comprises 6.02×10^{23} molecules (Avogadro's Number). So 4×10^{10} molecules represents 6.6×10^{-14} moles. We have said that for every millilitre of foam we have approximately 3,700 bubbles, so 20 mL of foam amounts to 74,000 bubbles. To coat all of them with a monomolecular protein layer would demand 4.9×10^{-9} moles.

Let us say that the content of relevant protein in beer is 0.1 g/L. Furthermore let us say that the mean molecular weight of this polypeptide is 10,000. Then the molarity of that polypeptide in beer is 1×10^{-5}. We have 20 mL of foam from 473 mL of beer. So in 473 mL of beer we have 4.7×10^{-4} moles of the relevant polypeptide. We have said that we need 4.9×10^{-9} moles to coat all the bubbles. So essentially we have a five-fold excess of the protein. There is vastly more protein in beer than is needed to coat bubble walls. On this basis we must conclude that it is not an issue of stoichiometry, but rather one of kinetics: how readily can the polypeptide enter into the bubble wall and, once there, undergo the changes necessary to stabilize the foam?

The rate of entry of polypeptides into the bubble wall

The theory of protein adsorption at gas-water interfaces has been summarized by Dickinson[10]. Basically it can be shown that the rate of change of extent of surface adsorption of a polypeptide is governed by the diffusion coefficient of the molecule (i.e. how quickly it can migrate), its concentration in the system (in this case, the bulk beer) and on the surface pressure, which is a measure of the extent to which the surface tension is lowered by the surfactant adsorbing at the interface ($\gamma_0 - \gamma$, where γ_0 is the initial surface tension and γ is the surface tension after addition of the agent).

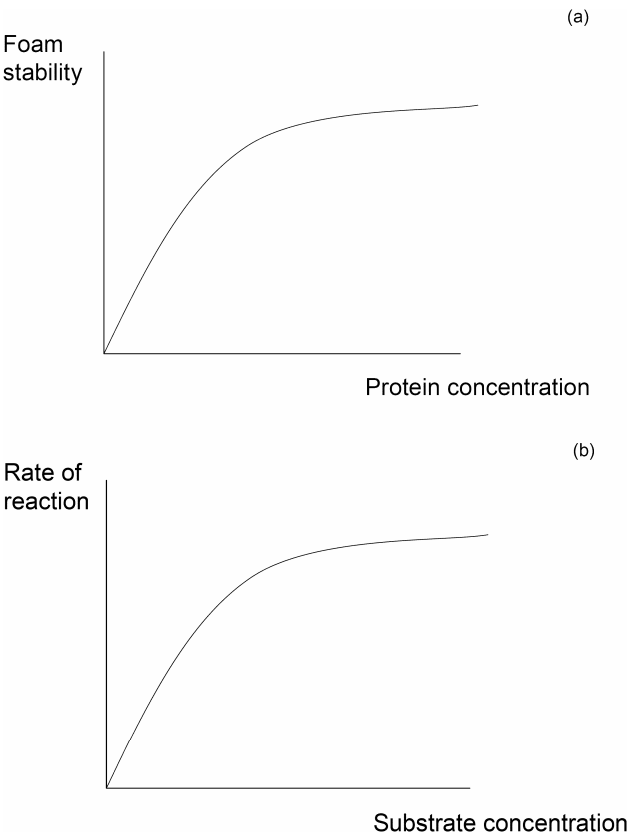

Fig. 1. The relationship between measured foam stability and polypeptide concentration (a) mirrors that of the impact of substrate concentration on the rate of an enzyme-catalysed reaction (b).

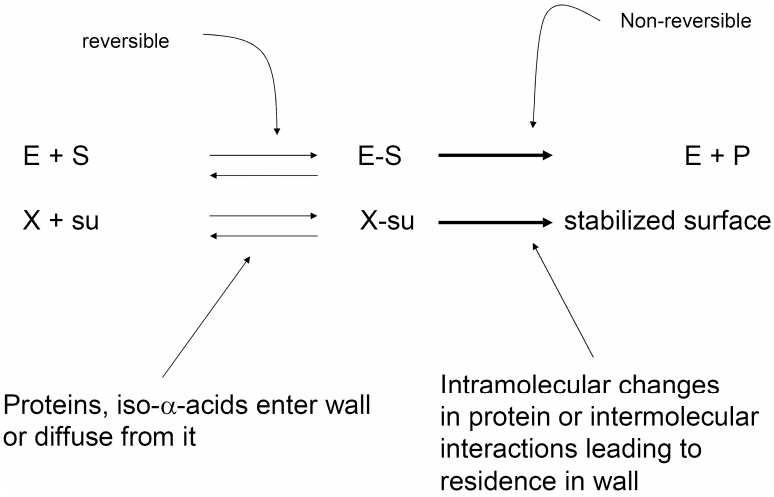

Fig. 2. The rationale for the hyperbolic plot observed for enzyme-catalysed reaction (Fig 1b) is that there is a reversible interaction between the surface of the enzyme (E) and the substrate (S), but at a sufficiently high substrate concentration all of the available sites on the enzyme are filled, and the enzyme is operating at maximum rate, which is determined by the rate at which the complex breaks down to reform the enzyme and release product (P). The analogous situation for foam would be if we consider the bubble surface (X) as being the equivalent of the enzyme surface, there being a reversible entry and departure of the surfactant molecules (su) to it. Changes can occur in the bubble (e.g. deformation of a polypeptide, interaction of the polypeptide with other components such as bitter acids) that leads to a stabilized surface. The hypothesis says that once all of the available space for the surfactant is occupied on the bubble (i.e. it is saturated) then the foam stability *for a given polypeptide* is maximized.

Thus

$$d\Gamma/dt = c(D/\pi t)^{1/2}$$

where

Γ = surface excess (by adsorption) (mol m^{-2}; kg m^{-2})

c = initial bulk protein concentration (mol m^{-3}; kg m^{-3})

D = diffusion coefficient (m^2 s^{-1})

π = surface pressure (N m^{-1})

t = time (s)

Whilst strictly speaking this equation only applies at the very earliest stages, when there is very little protein already at the interface, we can usefully integrate the equation to arrive at an expression for the surface excess

$$\Gamma = 2c(Dt/\pi)^{1/2}$$

Let us say we have a polypeptide present at 0.1 g per litre and that protein has a diffusion coefficient of 10^{-6} m^2 s^{-1} (proteins tend to have values in the range 10^{-7} to 10^{-6} m^2 s^{-1}, with increased D accompanying decreased molecular size[5]; insulin with molecular weight 41,000 has a D value of 8.2×10^{-7}). If the surface tension drop (π) caused by that protein is 30 N m^{-1}, then after 1 second Γ becomes approximately 3.4×10^{-8} kg/m^2. We have already performed a calculation suggesting that the surface area in our beer foam (bubble radius 0.4 mm) is 2.01 mm^2 per bubble. Converting the Γ value, we arrive at 3.4×10^{-11} g/mm^2 – i.e. approximately 7×10^{-11} grams of protein per bubble. We have said that there is space for 6.6×10^{-14} moles and we have assumed a protein molecular weight of 10,000, i.e. there is space for 6.6×10^{-10} grams of protein. Accepting that we have made several assumptions in the various calculations performed, we can nonetheless infer that at the 0.1 g per litre protein in beer, the surface coating represents perhaps a tenth of maximum. At 1 g per litre then we would expect that we are essentially "saturating" the bubble wall. Readers may satisfy themselves that these estimates are within the realm of actual observations by comparing this calculation with actual data – see later (Fig. 4).

The kinetics of foam stabilization in beer

If a simple experiment is performed whereby foam stability is measured in relation to a varying protein concentration, then it is customary to see a relationship of the type illustrated in Fig 1. Such a pattern can be readily explained in a manner exactly analogous to that of enzyme kinetics, whereby we substitute "bubble surface" for "enzyme" (Fig. 2; see also [2]). There is a reversible interaction of the foaming polypeptide with the bubble wall – that is, it can enter and leave the wall. As the concentration of polypeptide increases there is an increased tendency of the bubble wall to be filled with polypeptide at any instant. Eventually however there is a saturation point, whereby any additional polypeptide has no impact on foaming. The other component to the model is that irreversible interactions occur within the bubble, of the types described earlier (unfolding, interactions), that lead to a stabilization of the foam matrix.

Just as for enzyme kinetics we can construct double reciprocal plots (Fig. 3), from which we can compute two values – the maximum foam stability (F_{max} – it will be

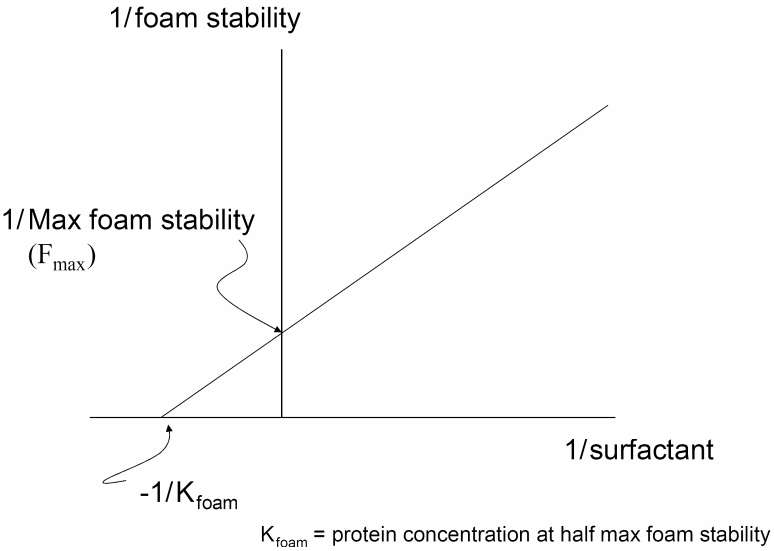

Fig. 3. The use of a double reciprocal plot to measure maximum foam stability and the affinity of a polypeptide for the foam.

noted that this is the foam stability with 1/protein is zero – i.e. protein is as high as it can get) and the K_{foam} value, which is the concentration of protein that gives half the maximum foam stability. The lower is K_{foam}, the greater is the tendency of that polypeptide to enter into the bubble wall.

The challenges of developing and interpreting this model are not insignificant. Whereas most kinetic analyses of enzymes are performed using individual purified enzymes and single substrates, for beer we have a complex mixture of the analogous molecules – i.e., a plethora of surface active species. The equivalent for enzyme kinetics would be trying to make sense of a situation whereby we had an ill-defined mixture of substrates and inhibitors.

In order to bring some order to the situation for beer foam, recent studies in this laboratory have focused on isolating proteins from barley on the basis of their solubility (albumins and hordeins) and subsequently partially hydrolyzing them to mimic the proteolysis that occurs in malting and (debatably) mashing[3,4,14]. Using the preparations made in this work[4] we can compute foam parameters as given in Table II. The low foaming ability (and limited solubility) of unhydrolysed hordein precluded us from generating values for it. However it will be readily apparent that the maximum foam stability achievable with the albumin preparations was substantially greater than for the hordein. Indeed, partial hydrolysis of the latter actually increased its ultimate foam stabilizing capability (F_{max}). However such hydrolysis increased the K_{foam} value, which means that after hydrolysis albumin has an inherently lesser tendency to enter into the bubble. Furthermore, the hydrolysed hordein had the lowest K_{foam} value of the three samples tested, indicating that it will preferentially enter the bubble wall if present in a mixture with albumin. This will mean that we would predict the net foam stability in a mixed system to be dictated by the presence of hordein. It will have the greater foamability and "squeeze out" the protein with the better foam stabilizing capability (see above). That this does actually occur is illustrated in Fig. 4. Thus for any beer the net foam stability will on the *balance* of the polypeptide species present, viz. the hydrolyzed hordeins and also the various proteins (all albumin-derived) that have been championed for their function in stabilizing foams, e.g. the 40,000 molecular weight protein Z[11] and Lipid Transfer Protein[6]. This is the likeliest explanation for the apparent decrease in foam stability reported to occur in beers from overly-modified malts, despite the fact that the level of foam active proteins derived from hordein increase in level as a result of proteolysis during the germination of barley[17].

It must be stressed that we are greatly simplifying the situation in these arguments, for example there is no discussion of the tendency of other surface-active species (e.g. iso-α-acids) to enter into foam and their ensuing interactions with polypeptides.

Table II. Foam parameters.

	K_{foam} (mg/mL)	F_{max} (cm)
Hordein	—	—
Hydrolysed hordein	0.67	16
Albumin	1.4	46
Hydrolysed albumin	3.0	89

Foam was assessed by a shaking test in which the depth of foam surviving a stand of 30 minutes represents a direct index of foam stability.

CONCLUSIONS

What can we conclude from the above discussion if we are to systematically enhance the quality and quantity of our beer foams?

1. Nucleation sites of whatever source (scratches, endogenous particles, microbubbles generated in vortex dispense systems) should be uniformly as small as possible in order to generate a homogeneous display of the small bubbles that will afford the stablest foam, least prone to disproportionation.

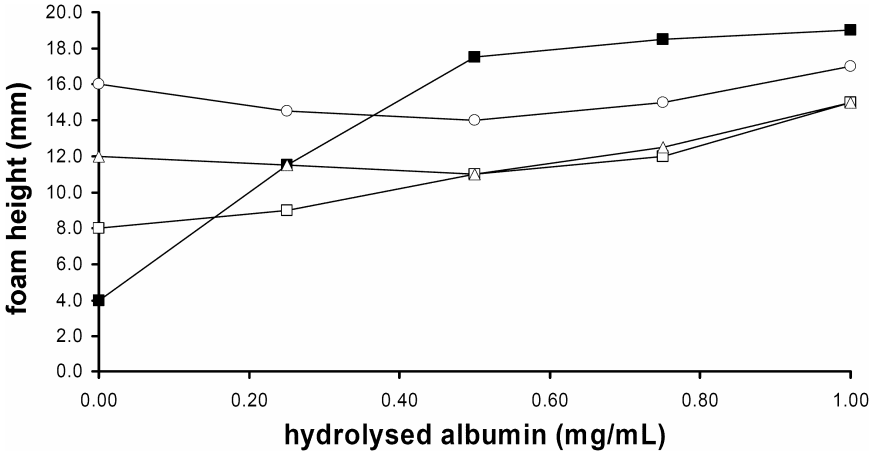

Fig. 4. Relationship of foam stability to hydrolysed albumin concentration at a series of fixed concentrations of hydrolyzed hordein (mg/mL): (■) 0.25; (□) 0.5; (△) 0.75; (○) 1.0.

2. Bulk surface tension is not a realistic variable. It will largely be determined by the alcohol content of a beer and this is not a legitimate variable for any given brand.
3. It is advisable to err towards the "top end of specification" for carbon dioxide in order to promote beading and creaming.
4. Enhanced "local" viscosity in the foam film will enhance film thickness by reducing drainage, which will in turn counter disproportionation. Such increases in localized viscosity would be most likely to be delivered by glycosylated proteinaceous complexes comprising a hydrophobic polypeptide component to deliver the species into the bubble, coupled to a substantial polysaccharide element that will both afford increased viscosity to limit liquid flow and physically maintain an increased distance between adjacent bubbles. As long ago as 1977, Bishop speculated that such materials were generated non-enzymically during the intense heating stages in malting and brewing[7].
5. Nitrogen has a major impact in reducing disproportionation. Low levels (e.g. 15–20 ppm) can exert this beneficial impact without the severe suppression of hop aroma and introduction of syrupy smoothness that is so detrimental to the flavour or many beer styles[12].
6. If it were possible to selectively eliminate hydrolysed hordein components from beer then this would be expected not only to enhance haze stability (see [21]) but also foam by eliminating species that preferentially enter into the bubble but have less foam-stabilizing capability once they are there. Perhaps selective proteinases[13] that act only on peptide bonds involving the prolyl residue so replete in hordein would be a worthwhile consideration.

ACKNOWLEDGEMENT

I thank Dr. Evan Evans (University of Tasmania) for valuable comments.

REFERENCES

1. Bamforth, C.W., Bringing matters to a head: the status of research on beer foam. *Proc. Eur. Brew. Conv. Cong. Foam Symp., Amsterdam,* Verlag Hans Carl, Getränke-Fachverlag: Nürnberg, 1999, pp. 10–23.
2. Bamforth, C.W. and Cope, R., Egg albumen as a source of foam polypeptide in beer. *J. Am. Soc. Brew. Chem.,* 1987, **45**, 27–32.
3. Bamforth, C.W. and Kanauchi, M., Interactions between polypeptides derived from barley and other beer components in model foam systems. *J. Sci. Food Agric.,* 2003, **83**, 1045–1050.
4. Bamforth, C.W. and Milani, C., The foaming of mixtures of albumin and hordein protein hydrolysates in model systems. *J. Sci. Food Agric.,* 2004, **84**, 1001–1004.
5. Barrow, G.M., Physical Chemistry. McGraw-Hill: New York, 1966.
6. Bech, L.M., Vaag, P., Heinemann, B. and Breddam, K., Throughout the brewing process barley lipid transfer protein 1 (LTP1) is transformed into a more foam-promoting form. *Proc. Eur. Brew. Conv. Congr., Brussels,* IRL Press: Oxford, 1995, pp. 561–568.
7. Bishop, L.R., The nitrogenous complexes of haze and foam and their measurement. *J. Inst. Brew.,* 1977, **83**, 350–355.
8. Clark, D.C., Mackie, A.R., Smith, L.J. and Wilson, D.R., Electrostatic interactions between proteins and their effect on foam composition and stability. In: Food Colloids, R.D. Bee, P. Richmond and J. Mingins, Eds., Royal Society of Chemistry: London, 1989, pp. 97–109.
9. Dickinson, E., Protein adsorption at liquid interfaces and the relationship to foam stability. In: Foams: Physics, Chemistry and Structure, A.J. Wilson, Ed., Springer-Verlag: Berlin, Heidelberg, 1989, pp. 39–53.
10. Dickinson, E., Murray, B.S. and Stainsby, G., Protein adsorption at air-water and oil-water interfaces. In: Advances in Food Emulsions and Foams, E. Dickinson and G. Stainsby, Eds., Elsevier: London, 1988, pp. 123–162.
11. Douma, A.C., Mocking-Bode, H.C.M., Kooijman, M., Stolzenbach, E., Orsel, R., Bekkers, A.C.A.P.A. and Angelino, S.A.G.F., Identification of foam-stabilising proteins under conditions of normal beer dispense and their biochemical and physico-chemical properties. *Proc. Eur. Brew. Conv. Congr. Maastricht,* IRL Press: Oxford, 1997, pp. 671–679.
12. Hughes, P.S. and Menneer, I.D., The relationship between sensory data and the composition of beer. *Proc. Eur. Brew. Conv. Congr., Maastricht,* IRL Press: Oxford, 1997, pp. 579–588.
13. Kabashima, T., Fujii, M., Meng, Y., Ito, K. and Yoshimoto, T., Prolyl endopeptidase from *Sphingomonas capsulata:* Isolation and characterization of the enzyme and nucleotide sequence of the gene. *Arch. Biochem. Biophys.,* 1998, **358**, 141–148.
14. Kapp, G.R. and Bamforth, C.W., The foaming properties of proteins isolated from barley. *J. Sci. Food Agric.,* 2002, **82**, 1276–1281.
15. Lynch, D.M and Bamforth, C.W., Measurement and characterization of bubble nucleation in beer. *J. Food Sci.,* 2002, **67**, 2696–2701.

16. Mohan, S.B., O'Shaughnessy, C., Shuttleworth, G. and Lyddiatt, A., Characteristics of beer proteins which affect foam stability. *Proc. Eur. Brew. Conv. Congr., Oslo,* IRL Press: Oxford, 1993, pp. 341–348.
17. Onishi, A., Proudlove, M.O., Dickie, K., Mills, E.N.C., Kauffman, J.A. and Morgan, M.R.A., Monoclonal antibody probe for assessing beer foam stabilizing proteins. *J. Ag. Food Chem.,* 1999, **47**, 3044–3049.
18. Prins, A., Principles of foam stability. In: Advances in Food Emulsions and Foams, E. Dickinson and G. Stainsby, Eds., Elsevier: London, 1988, pp. 91–122.
19. Prins, A. and van Marle, J.T., Foam formation in beer: some physics behind it. *Proc. Eur. Brew. Conv. Congr. Foam Symp., Amsterdam,* Verlag Hans Carl, Getränke-Fachverlag: Nürnberg, 1999, pp. 26–36.
20. Ronteltap, A.D., Beer foam physics. PhD thesis, 1989, Agricultural University, Wageningen.
21. Siebert, K.J. and Lynn, P.Y., Mechanisms of beer colloidal stabilization. *J. Am. Soc. Brew. Chem.,* 1997, **55**, 73–78.
22. Walstra, P., Principles of foam formation and stability. In: Foams: Physics, Chemistry and Structure, A.J. Wilson, Ed., Springer-Verlag: Berlin, Heidelberg, 1989, pp. 1–15.

(Manuscript accepted for publication October 2004)