Understanding foams & foaming [*]

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Most of the common foams are a two-phase medium of gas and liquid with a particular structure consisting of gas pockets trapped in a network of thin liquid films and plateau borders. Some well known foams are bubble baths, dishwater detergents and the foam head on beers. Many oils foam when trapped gas is suddenly released under conditions of an abrupt drop in pressure. In some refiners in which the through-flow of gas at high temperature and pressure is required to crack hydrocarbons, the gas-liquid mixtures will foam strongly. The foam traps gas with gas fractions of 80% or higher. Clearly in such situations, in which it is desired that solid catalysts contact liquids, the production of foam is not wanted. In other applications, foams are useful; for example foams which have a high yield stress and can be used in a fluid for carrying particles in applications ranging from the transport of cuttings in drilling and the placement of sands in cracks in oil producing reservoirs to increase the conductivity of reservoirs for secondary oil recovery. Obviously, bubble bath and shampoo companies should like to produce appropriate foams for dish and hair washing. Technologies which are impacted by foams and foaming are widespread.

Foams are not well understood and they are very hard to control. A foam cannot be created without the vigorous introduction of gas from a bubbly mixture. Bubble baths and dishwater soap won't foam unless gas is stirred in by a water jet or another mixing mechanism. Foaming oils won't foam unless the drop in pressure is sufficiently abrupt. To avoid a head of foam on beer it is necessary to pour the beer very slowly. To understand foaming it is necessary to try to be precise about the critical values of bubble release required to make and maintain a foam.

All static foams are unstable, but some are more unstable than others. The stability of foams is another subject in which our understanding is far from complete. Foams collapse by draining and film rupture. To keep a foam

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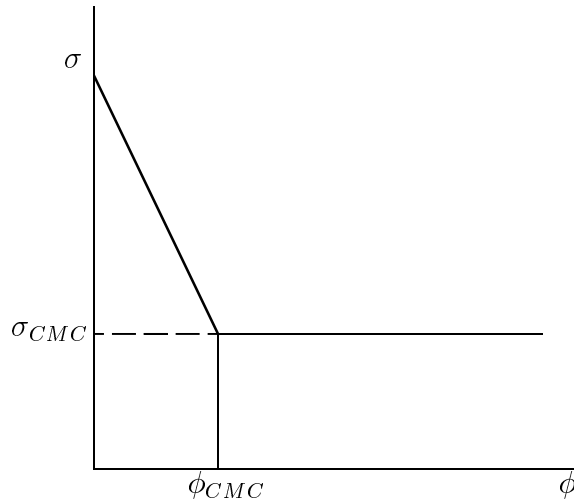
Figure 1: Surface tension σ versus bulk concentration ϕ. ϕ_{CMC} is the critical micelle concentration, σ_{CMC} is the maximally reduced surface tension. The bulk concentration is related to the surface excess by the Gibb's isotherm. The important quantity is the slope $d\sigma/d\phi$; we can get any slope even when the reduction of tension is not so great.

from collapsing it is necessary to oppose the draining by surface tension gradients induced by surfactants. It is not possible to get chemically pure liquids to foam; some contamination leading to surface tension gradients appears to be necessary even to create weak foams. Beers can give rise to big heads of foam which are relatively stable when the conditions are right. Champagne foams strongly when the conditions are right, but champagne foams are unstable and collapse rapidly. Cola drinks and water with gas produce bubbly mixtures, but they don't foam. To get a foam it is necessary to introduce gas into liquid, by a cavitation mechanism when gas is in solution, as in the examples above, or by gas injection as in dishwater soap and chemical reactors. The gas-liquid mixtures will foam only when surfactants are present to stabilize erupting bubbles. When a liquid does foam it may be described coarsely by its foaminess (ease of foaming) and stability (measured by time of collapse of foams).

There is a lot of confusion about the role of surface tension in foams and foaming. It is well known that some surfactants which reduce surface tension

greatly are not very effective in producing and stabilizing foam whereas others are indeed effective. The difference between good and poor surfactants appears to correlate more strongly with the rate at which surface tension changes with surfactant rather than how much it changes. To understand this we may consider a typical graph (Figure 1) of surface tension σ vs. surfactant concentration ϕ for, say: a system of surfactant plus water. In the ideal system the surface tension reduces linearly with ϕ until it plateaus at the critical value ϕ_{CMC} for micelle formation; when $\phi > \phi_{CMC}$ the new surfactant does not enter the already saturated fluid gas interface and instead enters into an association with other surfactant molecules in the bulk in a micelular arrangement in which hydrophobic heads come together trying to escape from the water. There are four distinguished values in figure 1; $\sigma(0), \sigma(\phi_{CMC}) = \sigma_{CMC}$ and ϕ_c, the critical micelle concentration. The slope of the surface tension graph

$$\frac{d\sigma}{d\phi} = \frac{\sigma - \sigma_{CMC}}{\phi_{CMC}}$$

can be very large, even when $\sigma - \sigma_{CMC}$ is very small, if ϕ_c is also very small. Actually $d\sigma/d\phi$ tells you how rapidly the crucial surface tension gradients develop when the surfactant mixture is stirred. The Gibbs elasticity may be defined in several ways; it could be regarded as a dimensionless expression for the rate of change of surface tension. One common definition is

$$Eg = A\frac{d\sigma}{dA}$$

where dA/A is a strain based on the change of the area of the surface. Actually σ cannot depend directly on A since A is neither a thermodynamic nor a material variable. Eg is defined strangely and needs interpretation. We may write:

$$\frac{d\sigma}{dA} = \frac{d\sigma(\phi)}{d\phi}\frac{d\phi}{dA} \tag{1}$$

Obviously $d\sigma/d\phi$ is a well defined concept and we think that the bulk concentration ϕ evaluated on the surface is changed when you change the area of the surface. Evidently we can express A in terms of the surface molar concentration. For a fixed number of moles

$$\frac{dA}{A} = \frac{d,}{,}$$

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$$Eg = , \frac{d\sigma}{d\phi} \frac{d\phi}{d,}$$

$d, /d\phi$ is a derivative which expresses how fast the surface excess concentration changes when you change the bulk concentration evaluated at the interface. It is related to the area/molecule. From area/molecule we can calculate the percent of the surface covered by surfactant. People who study the stability of foams and emulsions generally come to the realization that Gibbs elasticity is one of the most important parameters for distinguishing foaming properties of one surfactant solution from another.

Guitián & Joseph [1997] found that the CMC is not important in the foaming of their reactor. They suggest that the violent turbulent motions in the fluidized bed are always stretching surfaces, exposing fresh surface to the surfactant solution so that the effects of saturation are not seen.

Guitián & Joseph [1997] studied foam formation in a slit reactor when gas and water plus SDS injected continuously with injection rates given by the superficial gas velocity U_g and superficial liquid velocity, U_l. The reactor stood 170cm tall, 26cm wide with a depth of only 1.3cm, which allowed for very easy flow visualization. They found a critical condition for foaming

$$U_g \approx aU_l + b \tag{2}$$

where a and b depend on the foam quality and not on the velocity. You don't get foam when U_l is larger than a critical value depending on U_g; when U_l is fixed, there is a critical U_g at which foam just appears at the top of the reactor. If you increase U_g more, the foam pushes down consuming more and more of the reactor until the whole reactor is in foam with a gas fraction of over 84%. They got the same graph of gas holdup U_g in a commercial (CANMET) reactor using hydrocarbons at a temperature in the range of 400°C; the aqueous cold slit reactor can be used to study real refiners of hydrocarbons at high temperature and pressure.

The foaming criterion (2) is an example of a critical condition for foaming, it is a measure of the rate of bubble release required to form foam; when $U_g < b$, there is no foam at the top of the bubbly mixture even when $U_l = 0$. The foam always appears on the top and pushes down; it's like the head on beer which is lighter than the bubbly mixture below so that the foam and bubbly mixture are strictly segregated by gravity, foam above and bubbly mixture below.

The interface between the foam and the bubbly mixture can be very sharp (see figure 2) with discontinuous values of the gas fraction ε_g and gas velocity
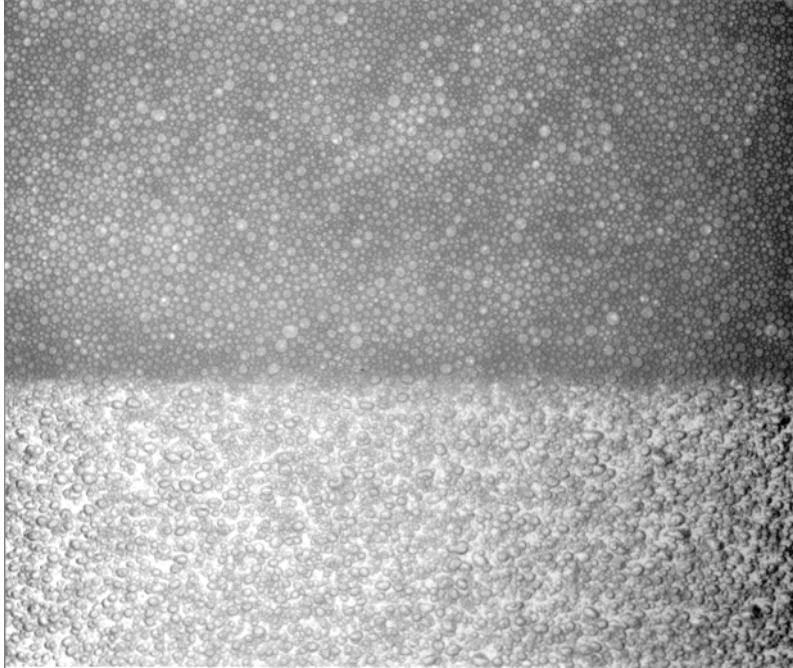
Figure 2: Foam interface between a bubbly mixture (below) and foam (above). The gas velocity is 4 cm/sec and the liquid (SDS + Butanol in Water) is 0.2 cm/sec.

$(U_g/\varepsilon_g = u_g)$. The interface that appears there is a phase change interface, foam above. We are dealing then with a two-phase, two-phase flow; the bubbly mixture with gas and liquid differs in "crystalline" microstructures from the gas and liquid in the foam. This interface is a great mystery and no one has as yet presented a plausible theory for it. Clearly, above a certain height, the gas and liquid are more comfortable in the foam phase.

Somehow the interface on the head of beer seems less mysterious than the interface in the Guitian-Joseph slit reactor shown in figure 2. The only difference between the reactor and beer is that gas bubbles come out of the solution because of thermodynamics, rather than being injected continuously as in figure 2. The interface below a head of beer also drops when the beer foams strongly; beer drinkers know that there is a lot of liquid in the head. The alcohols and other surfactant chemicals in the beer stabilize films on

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bubbles which rise to the interface below the head and the bubbles pack and distort into the close-packed arragement of films and plateau borders found in foams. The so called "foamy" oils which exhibit an anomalously high rate of primary recovery and production are something like a very viscous beer in which gas bubbles rise very slowly.

An invention would be to make a reactor in which terrestrial gravity is replaced by swirling gas, and liquid injected continuously outside would foam under a condition like (2), but the foam would segregate at the center where it could be removed. If solid particles were present as is required in cases where catalyst particles are required, they would also centrifuge in the bubble mixture, avoiding foam.

The cold slit reactor used by Guitián and Joseph was designed to study how solid particles could suppress foam. The motivation was that foam control in the patented HDH process could not be done with commercial defoamers like silicon oils which are degraded at the high pressures and temperatures at which these hydrocarbon crackers work. They found that solid particles would suppress formation of foam but did not understand the controlling features, size, weight and solids concentration. They thought, following the literature, that the mechanism by which solid particles suppress foam is by breaking foam and hydrophobic particles are required.

An entirely different mechanism of foam suppression was found by Guitián and Joseph [1997], foam control using a fluidized bed. Hydrophilic particles fluidized in the bubbly mixtures below the foam suppress foam formation dramatically without breaking the foam. The suppression is not perfectly understood but it occurs because the particles don't fluidize in the foam. The particles in the fluidized bed expand when the gas flow is increased, probably according to some rule of hindered settling. The expansion of the particles in the bubbly mixture pushes the liquid plus particles against the foam which at the same time is pushing down by increased foam formation due to more gas. The bed expansion opposes the foam formation and in some cases the expansion dominates and the foam retreats. Fluidized solid particles are at zero order, stationary objects like walls over which liquid must pass. Since these particles are hydrophilic the water "sticks" to them, increasing liquid holdup in the bed; its all in the data.

Another effect of solid particles is to increase the effective density of the bubbly mixture. In this case the buoyancy is proportional to the difference between the gas density and the density of the fluid plus solid mixture, which is larger than what you might guess using the liquid density. The gas then
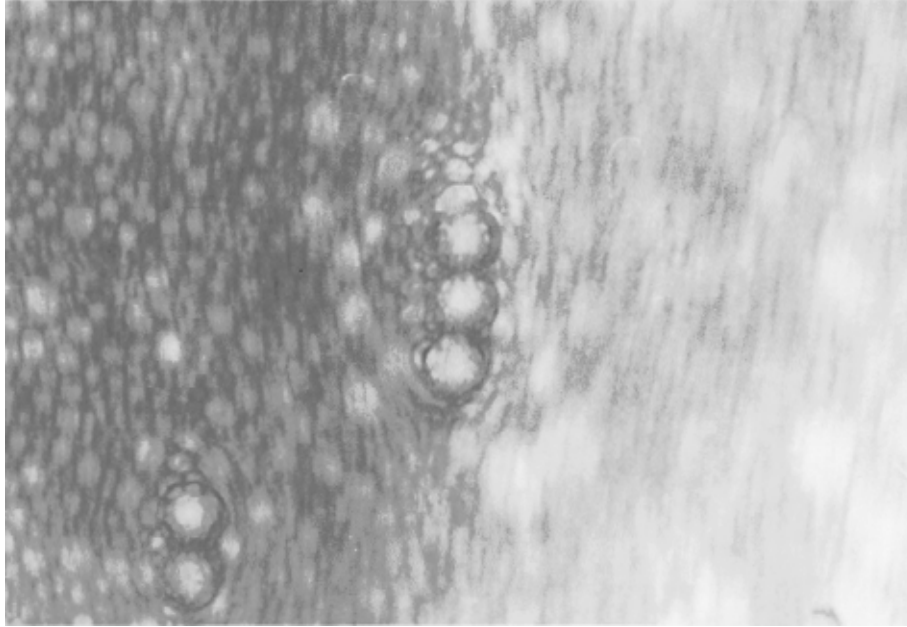
Figure 3: Particles falling in the foam tend to chain as in viscoelastic fluid.

is impelled to rise at a faster velocity, decreasing the holdup of gas. This mechanism works in bubbly mixtures whether or not foam is present, and it works even when the particles are hydrophobic.

Mata & Joseph [1997] have done some studies of foam control using fluidized beds of hydrophobic particles which can attack foam. They found an appreciable reduction in gas holdup when hydrophobic particles of the same concentration, size, shape and weight as hydrophilic particles were used. In one case the gas holdup in the bubbly mixture with no foam present increased because some gas sticks on the particles. In another case the gas holdup in the bubbly mixture actually decreased. We can probably assume that the further reduction of foam is due to breakup of foam with hydrophobic particles. The fluidized bed mechanisms of foam suppression are just enhanced by foam attack resulting in improved performance.

The anomalous results on the effects of fluidizing hydrophobic particles in bubbly mixtures without foam have not yet been clarified. It is probable the degree of hydrophobicity of particles matters for foam attack - but the

degree of hydrophobicity is irrelevant to the fluidized bed mechanism.

Foam rheology is another important subject for applications which is not well understood. Foams can trap and immobilize small and light particles showing that foams have an effective yield stress; this property makes foam a good drilling fluid for carrying away cuttings in underbalanced drilling. The foam flows, so there is some kind of viscosity for flow after yield but particles won't circulate in the foam and the foam itself does not circulate as an ordinary fluid. Heavy particles, driven into the foam by turbulence in the bubbly mixture fall out of the foam in a chain of linked particles (figure 3) characteristic of polymer solution. This shows that the foams have viscoelastic properties like polymeric solutions. Neither man nor beast, the true nature of foams has yet to be revealed.

References:

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