LIQUID DISTRIBUTION AND ELECTRICAL CONDUCTIVITY IN FOAM

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Abstract---Experiments were conducted with aqueous foam generated by bubbling nitrogen through anionic, cationic and nonionic surfactant solutions. The ratio of the electrical conductivity of the foam to that of the liquid was found to increase monotonically with the volumetric liquid fraction in the foam. The choice of surfactant as well as the degree of inhomogeneity in bubble size were found to be without effect on the relationship. However, for a fixed liquid fraction, it was found that decreasing the mean bubble size can decrease the conductivity ratio somewhat, as well as accelerate the approach toward Lemlich's limit for low density foam. This effect was attributed to increased suction within the Plateau borders.

INTRODUCTION

A foam is a dispersion of gas bubbles in a liquid wherein the liquid occupies no more than a modest volumetric fraction of the whole. The shape of the bubbles depends on this fraction which is a volumetric density. In a foam with a sufficiently high density, the bubbles tend to be rounded. This roundness can be retained even at lower densities provided the foam has a wide distribution of bubble sizes so that small bubbles can fit between larger bubbles. However, at sufficiently low density, the bubbles press against each other and assume a more polyhedral shape.

Since the gas phase is electrically nonconducting, an electric current will pass only through the liquid phase. Hence the electrical conductivity of the foam as compared to that of the corresponding bulk liquid is an important and useful property which can serve to characterize the liquid content in the foam. However, the bubble sizes and the nature of the surfactant are also parameters which might affect the relationship. The possible effect of these parameters has not received much attention in the past. Accordingly, the present study was undertaken in order to investigate these matters and to shed some light on the detailed structure of foam, especially the relative distribution of interstitial liquid between lamellae (films between polyhedral bubbles) and Plateau borders (channels formed by the intersection of lamellae).

PREVIOUS WORK

Theoretical analyses have been reviewed and developed by Chang & Lemlich (1980) and by Agnihotri & Lemlich (1981). These cover high density foams of spherical bubbles as well as low density foams of nearly polyhedral bubbles.

Conduction through polyhedral foam takes place partly along the lamellae but primarily along the Plateau borders since, due to interstitial suction, the Plateau borders are where most of the liquid resides. For the theoretical limiting case wherein all the interstitial liquid is in the Plateau borders, Lemlich (1978) derived

$$
D=3K
$$
 [1]

where D is the volumetric density of the foam and K is the conductivity of the foam divided

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by the conductivity of the continuous phase which for present purposes is liquid.[†] Equation [1] is approximated by a real foam of extremely low density.

By way of contrasting comparison, Agnihotri & Lemlich (1981) derived [2] for the hypothetical complementary limiting case wherein the continuous phase is entirely in the lamellae.

$$
D = 1.4K. \tag{2}
$$

Then, by recognizing that lamellae and Plateau broders form a complex bridge circuit, they derived $[3]$ for F which is defined as the fraction of interstitial liquid that effectively resides in the lamellae.

$$
2.625(D/K)^{-1} - 0.875 < F < 1.875 - 0.625D/K. \tag{3}
$$

 $1 - F$ is the fraction in the Plateau borders. Finally, for lack of a better estimate, they arithmetically averaged the two bounds of the inequality and obtained [4] as an approximation for F.

$$
F = 1.3125(D/K)^{-1} - 0.3125(D/K) + 0.5.
$$
 [4]

Experimental studies include the investigation by Miles *et al.* (1945), the classical work of Clark (1948), the early work by the present authors' group peripheral to other studies which is summarized by Jashnani & Lemlich (1975), the work of various authors summarized by Chistyakov & Chernin (1977) including their own, and the results of Chang $\&$ Lemlich (1980).

In this last study (which involved only nonionic surfactants), a convenient "snatching" technique was devised in which foam was steadily passed up through a vertical glass column fitted with a quickly removable test section of known volume containing the conductivity cell. After the conductivity of the foam was measured, the test section was snatched from the column and quickly net weighed. Then, with the conductivity and specific gravity of the liquid having been previously measured or already known, both D and K were readily obtained. Accordingly, the present study employed the snatching technique, but with certain improvements as outlined in the next section.

EXPERIMENT

The apparatus was of Pyrex glass with rubber gaskets and O-rings. Fluid lines were of Tygon. Figure 1 shows a schematic diagram.

Nitrogen from a gas cylinder was passed through control valves, a rotameter, a surge vessel, a humidifier, and a sparger, to form bubbles in a pool of liquid which consisted of water, surfactant, and for some runs glycerine and/or electrolyte. The bubbles rose to form a foam which ascended continuously through a cylindrical test section and into a collecting vessel from which collapsed foam was returned to the pool. A stream of liquid was withdrawn from the pool and pumped to an overhead constant head vessel which, in turn, provided an adjustable steady liquid feed to the top of the vertical column of foam. Changing the rate of this feed from run to run permitted a corresponding change in foam density.

The test section was 40.6 cm long and 4.67 cm in i.d. It was held snugly in place by means of rubber gaskets and rubber bands at each end, yet was easily released for

tin the literature the word "conductivity" is sometimes employed in place of the word "conductance", partly because the conductance ratio in a given cell is equal to the conductivity ratio.

Figure 1. Apparatus (not to scale).

snatching. The section was equipped internally with three flush-mounted 25.8 cm^2 platinized platinum electrodes as shown in figure 1. These electrodes were considerably larger than those employed by Chang $\&$ Lemlich (1980) and thus offered assurance that, even with fairly large bubbles, the foam was sensed as a continuum.

The diagonal pair of electrodes was deemed to offer the most representation conductive path and, accordingly, was used for the determination of K. However, for the sake of comparison, measurements were also taken over the other two possible paths, namely, horizontally and vertically.

A properly prepared glass capillary tube gives a succession of bubbles of uniform size as long as the gas flow rate is within a certain suitable range (Brunner $\&$ Lemlich 1963). Accordingly, glass capillary tubes with i.ds of 0.15, 0.73 and 1.35 mm, and lengths of 15, 25 and 20 mm respectively were used to make up the spargers. The ends of each tube were carefully ground smooth with very fine emery paper. Also, in some runs an extra-coarse sintered glass frit was employed to generate a wide and essentially continuous distribution of bubble sizes.

For each run, an aqueous solution of one of the following three surfactants was employed: Triton X-100 (scintillation grade, Eastman Kodak Co.) which is nonionic, hexadecyltrimethylammonium bromide (certified A.C.S. grade, Fisher Scientific Co.) which is cationic, and sodium lauryl sulfate (laboratory grade, Fisher Scientific Co.) which is anionic. Glycerine (U.S.P. 96%, Chemicals Inc., Cincinnati, Ohio) was added in some cases to increase viscosity and thus maintain sufficient foam stability in the test section. Potassium chloride (Baker analyzed reagent, L. T. Baker Chemical Co.) was added to give a concentration of 0.04 M in the nonionic and cationic surfactant systems so as to impart sufficient conductivity for convenient measurement.

However, both KCI and NaC1 caused precipitation in the anionic surfactant system. Accordingly, for this last system 0.03 M sodium lauryl sulfate was used without any additional electrolyte. This contrasts with 0.001 M surfactant for the other two surfactants which did involve the use of added electrolyte.

Conductances of foam and liquid were measured with a Beckman RC-19 a.c. conductivity bridge at 1000 Hz, and double checked from time to time with a Beckman RC-18A conductivity bridge which could be operated at 1000 Hz and 3000 Hz. A General Radio 631-B strobotac was used to measure the frequency of bubble generation stroboscopically. Photographs of the pool and foam were taken on Kodak PX-135 (100 ASA) black and white film with an Asahi 35 mm Pentax MX camera fitted with an f/4 100 mm macrolens and helicoid extension ring. Illumination was provided by a Vivitar-200 electronic flash.

Further details are on file (Datye 1980).

RESULTS AND DISCUSSION

Preliminary experiments showed that the conductivity and specific gravity of collapsed foam were essentially equal to the corresponding properties for the pool liquid. All conductivity measurements were normalized for the effect of temperature.

Foam with nearly uniform bubbles was generated by employing three identical capillary tubes as bubblers simultaneously. Figure 2 shows such an example. Foam with nonuniform bubbles was generated by using tubes of differing i.d., or by using the sintered glass sparger.

In nonuniform foam, a disproportionately large number of small bubbles appeared at the glass wall. This accords with similar observations from a recent investigation (Cheng & Lemlich 1983). The effect of such physical segregation is to counter the effect of planar statistical bias at the wall (Clark & Blackman 1948; de Vries 1957, 1972) and thus to call into question the advisability of employing at the wall the correction formula for such bias (Jashnani & Lemlich 1974). This has important implications for studies that involve the accurate determination of bubble size distributions in foam by visual or photographic measurement at a retaining wall.

Figure 2. A foam of nearly uniformly sized bubbles produced by bubbling through three identical vertical submerged capillary tubes, each of 0.15 mm i.d.

Further discussiori of foam bubble segregation and nonuniformity at a wall is beyond the scope of the present study. It is dealt with elsewhere (Cheng & Lemlich 1983).

Most of the bubbles in the pool appeared to be approximately oblately spheroidal shortly after release. Accordingly, the bubble diameter was taken to be that of a sphere equal in volume to a spheroid. For large uniform bubbles, the diameter so obtained averaged 17% lower than the diameter calculated from gas flowrate and bubble frequency. For small uniform bubbles it averaged 13% lower.

Figure 3 shows results obtained with the sintered glass for the three types of surfactant system. The plot shows that the choice of surfactant had very little effect on the conductivity of the foam, even when the concentration was changed by a factor of 30 from 0.001 M for the nonionic and cationic surfactants to 0.03 M for the anionic surfactant. The analogous results (omitted for the sake of brevity) with uniform bubbles from the capillary tubes confirm this.

The presence of small amounts of glycerine was also without significant effect. This was tested up to concentrations of 6 vol. $\frac{6}{10}$.

In figure 4 the present results with sintered glass are compared against the corresponding results of Chang & Lemlich (1980) also obtained with sintered glass. Agreement is good. D increases monotonically with K according to an essentially unique relationship. Thus, for a sintered glass sparger, figure 4 can be used to correlate D with K .

Figure 5 shows the parametric effect of bubble size with the anionic surfactant. For a given K , it is evident that D increases as bubble size decreases. In particular, approximately halving the mean bubble diameter from 3.13 to 1.63 mm increases D by roughly 8% .

Figure 3. Results for polydispcrsc foam generated by an extra-coarse sintercd **glass sparger,** illustrating reproducibility despite differing types of surfactant: \triangle , nonionic; \Box , cationic; \times , anionic.

Figure 4. Comparison of present results with those of Chang & Lemlich (1980), all for polydisperse foam generated by an extra-coarse sintered glass sparger: \triangle , present results; \Box , Chang & Lemlich.

Figure 5. Results with 0.03 M sodium lauryl sulfate and 0–6 vol. $\%$ glycerine, illustrating the effect of bubble size. \triangle , Large bubbles: mean diameter = 3.13 mm, standard deviation = 0.10 mm; \Box , small bubbles: mean diameter = 1.63 mm, standard deviation = 0.06 mm.

Within each run of figure 5 the bubbles were quite uniform in size, having been generated by either three 0.73 mm i.d. capillary tubes or three 0.15 mm i.d. capillary tubes. The standard deviations were only 3% and 4% respectively. Thus the parametric effect is clearly due to change in the mean bubble size and not due to any effect associated with nonuniformity of bubble size. Similar results (not shown here) were obtained with the other two surfactants.

All this is further confirmed by figure 6 with the anionic surfactant. Here results for uniform foam are compared with those for nonuniform foam. The respective mean bubble diameters of 3.13 and 2.84 mm are very close to each other, differing by only 10% . On the other hand, the large standard deviation of *0.99* mm for the nonuniform foam is 10 times the standard deviation of the uniform foam. Nevertheless, figure 6 reveals no significant effect of this nonuniformity. Corresponding results were obtained with the other two surfactants. Accordingly, the aforementioned parametric effect is due solely to mean bubble size.

The present authors suggest that the reason for this effect of mean bubble size involves the surface tension, γ , and the curved triangular shape of the cross section of a Plateau border, as illustrated in figure 7. If D is held constant while bubble diameter is decreased, the linear dimensions of the Plateau border cross section will not decrease in proportion. This is because the decrease in the radius of curvature, R, of the Plateau border increases the suction pressure, ΔP , in the Plateau border. The governing relationship is the classical law of Laplace & Young which yields $\Delta P = \gamma/R$ for a Plateau border (Leonard & Lemlich 1965).

The increased suction draws more liquid from the lamellae into the Plateau borders thus increasing their conductance at the expense of conductance along the lamellae. The

Figure 6. Results with 0.03 M sodium lauryl sulfate and 0-6 vol. $\%$ glycerine, illustrating the lack of effect of polydispersity. \triangle , Uniform bubbles: mean diameter = 3.13 mm, standard deviation = 0.10 mm; \square , nonuniform bubbles: mean diameter = 2.84 mm, standard deviation = 0.10 mm; \Box , nonuniform bubbles: mean diameter = 2.84 mm, standard $deviation = 0.99$ mm.

Figure 7. Plateau border, P, with lamellae, L, showing radius of curvature, R.

overall effect on the foam is a greater influence of [1] with its higher coefficient of 3 and a diminished influence of $[2]$ with its lower coefficient of 1.4. The net result for a given D is a lower K , or for a given K the result is a higher D as reported above.

The effective redistribution of intersititial liquid is presented quantitatively in Table 1 which shows some typical approximate values for F from [4]. Upper and lower bounds for F from [3] are also given. It is clear that for a given D , the smaller the mean bubble diameter is, the smaller is the value of F and hence the larger is the value of $1 - F$. Thus the smaller the mean bubble size, the greater is the portion of interstitial liquid in the Plateau borders.

Table 1 also confirms the decrease in F and thus the increase in the portion of liquid in the Plateau borders that occurs as D decreases. The concomitant result is a closer approach to [1].

This approach to $[1]$ is clearly illustrated in figure 8 which shows results at low D for all three surfactants. The small bubbles were generated by the sintered glass sparger and the large bubbles were from the three 0.73 mm i.d. capillary tubes. It is evident from figure 8 that, as D decreases, the results more closely approximate the limit previously proposed by Lemlich (1978). Furthermore, the approach is more rapid with the smaller bubbles. This, of course, is in accord with the discussion presented above.

In a recent paper, Sharovarnikov (1981) did not present values for K but did report a trend in absolute resistance measurements of foam that is equivalent to a decrease in D/K as D decreases. He attributed this trend to surface conductance along the lamellae. However, no such effect was found in the present study, either with or without the presence of the electrolyte KC1. As may be seen from careful inspection of each of figures 3-6 and 8, *D/K* increases as D decreases, even for the low D of figure 8 which is comparable to Sharovarnikov's low range. Nevertheless, for an ionic surfactant in the absence of significant added electrolyte, appreciable relative surface conductance due to adsorption is theoretically a possibility provided D is sufficiently low.

Table 1. Typical results for F, the fraction (percentage here) of interstitial liquid that is effectively in the lamellae as a function of bubble size and volumetric foam density, D. Surfactant system: 0.03 M sodium lauryl sulfate with 0-6 vol. $\%$ glycerine

Sparger	Mean bubble diameter + standard deviation, mm	F.%	
		$D = 0.01$	$D = 0.05$
0.73 mm I.D. tubes	$3.13 + 0.10$	$22 \div 30 \div 38$	$39 \leq 48 \leq 58$
0.15 mm I.D. tubes	$1.63 + 0.06$	$14 \times 20 \times 26$	28 < 36 < 45
Sintered glass	0.95 ± 0.33	$9 \le 14 \le 18$	26 < 34 < 42

Figure 8. Results at low density with all three surfactant systems, showing the approach to Lemlich's limit as the density decreases: \triangle , sintered glass sparger; \times , three 0.73 mm i.d. tubes.

CONCLUSIONS

Volumetric foam density increases monotonically with the ratio of the conductivity of the foam to the conductivity of the continuous phase. The relationship is independent of the nature of the surfactant system and of the degree of nonuniformity in bubble size, at least over the range of variables investigated. However, it does depend somewhat on the mean bubble size. For a given conductivity ratio, the foam density can increase with a decrease in bubble size.

This effect of bubble size implies that, for a given volumetric foam density, a larger portion of the interstitial liquid effectively resides in the Plateau borders when the foam is composed of smaller bubbles. A probable explanation is the increased suction within the Plateau borders that stems from the interaction between surface tension and sharper curvature at smaller size.

For foam produced by an extra-coarse sintered glass sparger, the curve of figure 4 can be employed to correlate volumetric foam density with conductivity ratio.

At very low foam density and especially with foam composed of small bubbles, the results approximate Lemlich's limit for conduction solely through Plateau borders.

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