

# FOAMINESS MEASUREMENTS USING A SHAKER BOTTLE

by  
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## 1. INTRODUCTION

Foams are colloidal systems in which a gas phase is dispersed throughout a continuous liquid phase; the gas cavities are separated by thin liquid films which are stabilized in some way by surfactants. Pure liquids do not foam. A fundamental characteristic common to all foams is their very large interfacial area which is unstable in the thermodynamic sense. Some foams can exist for a long period of time in the absence of external disturbances while others collapse very fast when the gas flow producing foam is suppressed. The metastability of the liquid films determines the overall foam stability.

There are two extreme structures which foam can assume. These are the classical polyhedral and the almost round-bubbled or gas dispersion structure. Both types of foams can exist together and both can be found in a shaking bottle after a certain period of draining. Polyhedral foams (dry foams) have very high gas hold-ups ( $\epsilon_g > 95\%$ ) which are normally observed in continuous systems when the ratio of gas to liquid velocity in a continuous system is very high. In this case, the gas is separated by thin liquid films, generating a three dimensional structure, in which liquid drains from the foam under the influence of capillary forces and disjoining pressure. Almost round-bubbly foams or “kugelshaum” (Manehold 1953) are characterized by nearly spherical gas bubbles which are separated by relatively thick films as in a compressed bed of packed spheres. This

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foam type is characterized by a moderate gas hold-up ( $74\text{v}\% \leq \epsilon_g < 95\text{v}\%$ ) and is present at relatively low gas/liquid velocities.

The foam producing capability (*Foaminess*) cannot be explained by surface tension alone; foam formation is strongly dependent on the surfactant and the dynamics of the system. The *Foaminess* of a system has to be distinguished from and is generally unrelated to *stability* of a foam. Foam stability is related to the time it takes for the foam once created, to disappear. The degree of foaminess may be regarded as proportional to the initial volume of foam created by a given energy supply to the system. Thus, whereas a foam may possess a high foam stability it may exhibit a relatively small foaminess. Several methods for generating and characterizing small-scale foam are discussed by Bikerman (1973). The two methods most used are:

I.-Spargers. Gas is sparged inside a tube with a glass sinter at the bottom into which a known volume of test liquid is introduced. The flow of gas through the sinter causes the liquid to foam. The gas flow is measured by a rotameter; it determines the superficial gas velocity ( $U_g$ ) in the cylinder. Due to drainage, foam at the top dries until it reaches a critical film thickness for collapse, giving the maximum foam height ( $H_0$ ). Using this method, a foaminess index ( $\Sigma$ ) of the foam can be determined; this index is the ratio of foam volume generated by a given gas flow rate:

$$\Sigma = H_0 / U_g \quad (1)$$

II.-Shaker bottles. A fixed liquid/gas mixture in a bottle is shaken for a specified period of time. After shaking the bottle, an initial volume of foam is present. This is an indication of the foaminess of the solution. The time it takes for the foam to collapse can be called the foam collapse time.

Both of these tests are hard to standardize. For example, the bubble size distribution appears to have an effect on the collapse time (Rand et al. 1983) and can vary from experiment to experiment. Some procedures have been standardized using an

arbitrary set of guidelines for the design of the apparatus and the running of the experiments (Ross 1980); This does not mean that the method represents in general mechanisms of foam formation and collapse of a given system. These methods only can be used as reference tests to determine foam formation capability of different foaming systems.

## 2. SURFACE TENSION MEASUREMENTS.

The presence of surfactants is necessary for foaming to occur in aqueous and non-aqueous media. The experimental systems used in this investigation consisted of aqueous solutions containing one anionic or nonionic surfactant or mixtures. Ternary solutions also were selected because they represent the simplest systems where iterations between different type of surfactants can be evaluated. The surfactant agents we used are given in Table 1. There are many works in the literature on alcohols in water solutions using  $C_1$ ,  $C_2$ ,  $C_3$  alcohols. These alcohols have very high vapor pressure and when air is bubbled through, it can strip away the alcohol. To minimize this effect and to maximize foaming, 1-Pentanol was selected. According to Bikermann (1973), Pentanol has the maximum foam producing capability among the aliphatic alcohols. Triton X-100 was selected because previous works have shown that it has a high foam producing capability. The BisE<sub>8</sub> and BisE<sub>12</sub> are silicon surfactants whose foaminess is not well known although they have been studied extensively in the Chemical Engineering Department at the University of Minnesota. For the ionic surfactant SDS was selected, because of its strong capability for foam formation reported by Bikerman (1973).

The surface tension of the aqueous solutions of these surfactants was measured using the Precision Ring Tensiometer Censo No. 70535 and the values obtained by this method were checked against values from a Spinning Drop and Pendant Drop Tensiometer. Aqueous surfactant solutions were prepared using commercial distilled water. In order to

verify the calibration of the equipment, the surface tension of water was measured using a pendant drop (71.4 dyne/cm) and a spinning drop tensiometer. (70.8 dyne/cm). Both results were compared with the value obtained in the ring tensiometer at a temperature of approx. 22°C (71.15 dyne/cm).

Figure 1 shows the relationship between the surface tension of the mixtures SDS/1-Pentanol/water and SDS for different concentrations of 1-Pentanol. Surfactant concentration is given in wt%. As can be observed, when the concentration of surfactant increases, the surface tension of the mixture decreases to an apparently asymptotic value recognized as the critical micelle concentration or CMC.

The CMC is explained in terms of the formation of organized aggregates of large numbers of molecules called micelles, in which the lipophilic part of the surfactant are attracted to the interior of the aggregate, leaving the hydrophilic part to face the aqueous solution. A lower CMC is produced by increasing the molecular mass of the lipophilic part of the molecule, lowering temperature, and adding electrolyte. (Schramm et al. 1994). In the system Water/1-Pentanol/SDS (Figure 2) the CMC decreases as the 1-Pentanol concentration increases because of the increased amounts of alcohol solubilized in the micelle.

Surfactant Name	Purity [%]	Mw	Density [gr/cc]	Supplier
Sodium Dodecyl Sulfate (SDS)	98.0 (2% dodecanol)	288	0.8	Aldrich Chemical Co
1-Pentanol	99.0	88	0.824	Aldrich Chemical Co
BisE <sub>12</sub>	90	808	≈1.0	UMN
BisE <sub>8</sub>	90	633	≈1.0	UMN
Triton X-100	97	647	≈1.0	Aldrich Chemical Co

Table 1 Surface active agents used in the experiments.

Table 2 gives CMC values as a function of 1-Pentanol concentration; the measured values agree with values from the literature. The CMC for SDS without 1-Pentanol cannot be readily observed because the sample was contaminated with 2 wt% Dodecanol. Measurements of surface tension are very sensitive to contamination. This can be clearly observed in Figure 2 where the literature values of surface tension of pure SDS are compared with those in this investigation which contain 2 wt% dodecanol. Although both compounds are absorbed on the interface, the Dodecanol preferentially concentrates there because it is even more surface active than SDS. The micellation process also extends over a much broader concentration range creating the minimum value of surface tension observed near the CMC.

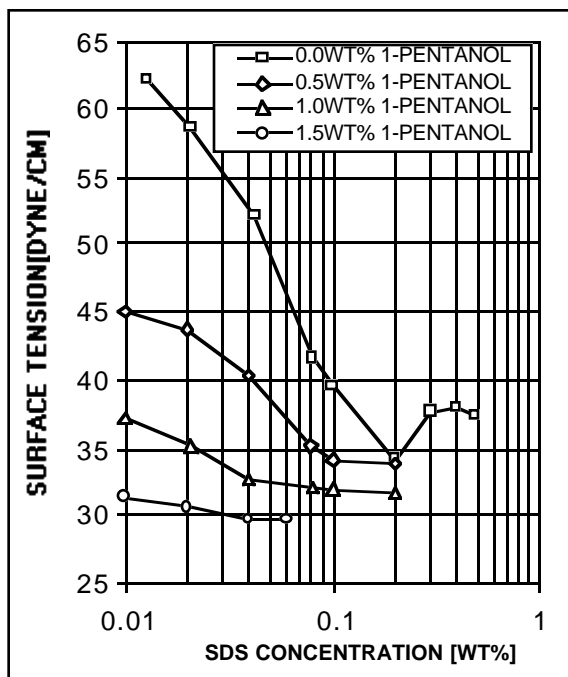


Figure 1 Relationship between Surface tension and SDS concentration in water at different 1-Pentanol concentrations. (Temp. = 22°C)

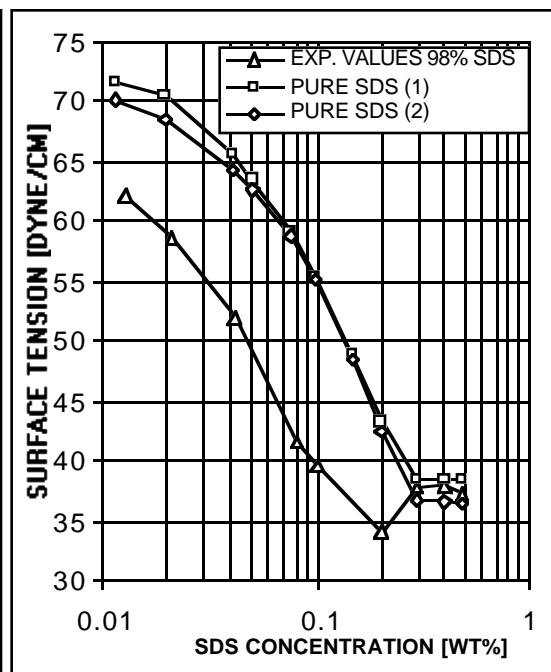


Figure 2 Effect of SDS purity on the relationship between surface tension and concentration.

(1) Mysels K. (1986) Surface tension of pure sodium dodecyl sulfate. *Langmuir*, 2, 423-442. (2) Evans D. and Wennerstrom H. (1994). *The colloidal domain: where physics, chemistry, biology, and technology meet.* VCH Publishers, New York.

If the SDS concentration is increased above the CMC, Dodecanol desorbs from the interface and is replaced by the SDS molecules. Therefore, the surface tension increases

to a value closer to the characteristic one for SDS above the CMC. Small amounts of impurities present in surfactants constitute a major obstacle in understanding this subject (Evans 1994).

Figure 3 shows the surface tension 1-Pentanol/water. As can be observed a concentration of 2 wt% of 1-pentanol is able to reduce the surface tension of the water from 71.15 dyne/cm to 28 dyne/cm indicating its high surface activity. The surface tension of pure 1-Pentanol is 23.5 dyne/cm at 22°C (Raid et al. 1968) with a maximum solubility in water at the same temperature of 2.7 wt% (Perry et al. 1973).

1-Pentanol Concentration [wt%]	SDS CMC [wt%]	SDS CMC Rao I. et al (1986) [wt%]
0.0	~0.2	0.227
0.5	0.09	0.09
1.0	0.05	0.037
1.5	0.04	-

Table 2 CMC of SDS as a function of C5OH concentration

Figure 4 shows the surface tension of the nonionic surfactants Triton X-100, BisE<sub>8</sub> and BisE<sub>12</sub> as a function of concentration. The lowest surface tension is obtained with BisE<sub>8</sub> with a CMC value of 21 dyne/cm.

The dependence of surface tension on concentration (wt%) using

$$\Delta\sigma = \sigma_s - \sigma = \Gamma_\infty R_g T L n \left( 1 + \frac{C}{a} \right) \quad (2)$$

Equation (3) was first found empirically by Szyszkowski (1908). It is based on the Gibbs equation for the adsorption of a surfactant in a interface with ideal solutions and the Langmuir adsorption isotherm. It applies only for concentrations lower than the CMC. For multicomponent system equation (2) has the form (Ross et al, 1983).

System	Equation Temperature: 22°C-23°C	CMC [wt%]	Range of application [wt%]	Regression Coefficient R <sup>2</sup>
Water/SDS	$71.15 - \sigma = 17.5127Ln\left(1 + \frac{C}{0.01988}\right)$	~0.2	0.0 ≤ C ≤ 0.15	98.0
Water/C5OH	$71.15 - \sigma = 15.60893Ln\left(1 + \frac{C}{0.1344}\right)$	2.7 Solubility limit	0.0 ≤ C ≤ 2.0	100.0
Water/SDS/C5OH	$71.15 - \sigma = 16.2767Ln\left(1 + \frac{C_{SDS}}{0.017098} + \frac{C_{C5OH}}{0.14964}\right)$	See Table 2	0.0 ≤ C <sub>SDS</sub> ≤ 0.15 0.0 ≤ C <sub>C5OH</sub> ≤ 1.5	99.8
Water/Triton X100	$71.15 - \sigma = 7.769226Ln\left(1 + \frac{C}{0.0000856}\right)$	0.017	0.0 ≤ C ≤ 0.017	99.9
Water/BisE <sub>12</sub>	$71.15 - \sigma = 6.323924Ln\left(1 + \frac{C}{8.991E(-6)}\right)$	0.0205	0.0 ≤ C ≤ 0.0205	100.0
Water/BisE <sub>8</sub>	$71.15 - \sigma = 6.63308Ln\left(1 + \frac{C}{4.8445E(-6)}\right)$	0.00929	0.0 ≤ C ≤ 0.00929	99.9

Table 2.1.2.5 Surface tension equations for the different foaming systems evaluated using (2) and (3)

$$\Delta\sigma = \sigma_s - \sigma = \Gamma_\infty R_g T L n \left( 1 + \sum_{i=1}^n \frac{C_i}{a_i} \right) \quad (3)$$

In general, these equations can be expressed with  $C/a_i$  in mole fractions or in weight fractions. Using a nonlinear regression program the constants for each system were evaluated. Table 3 shows the results for each system as well as the regression coefficient ( $R^2$ ).

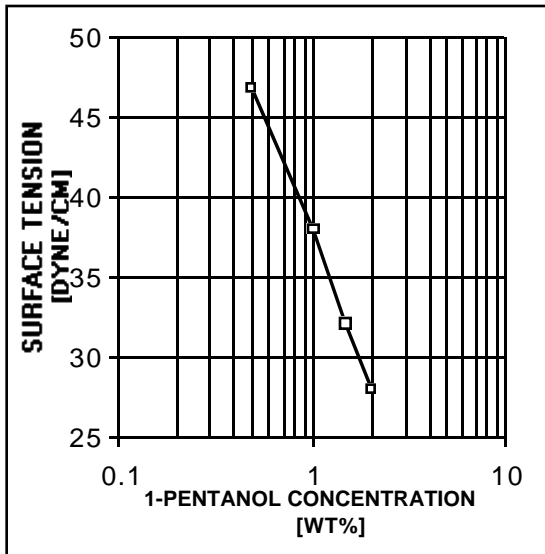


Figure 3 Surface tension of 1-Pentanol/water mixtures (Temp.= 22°C)

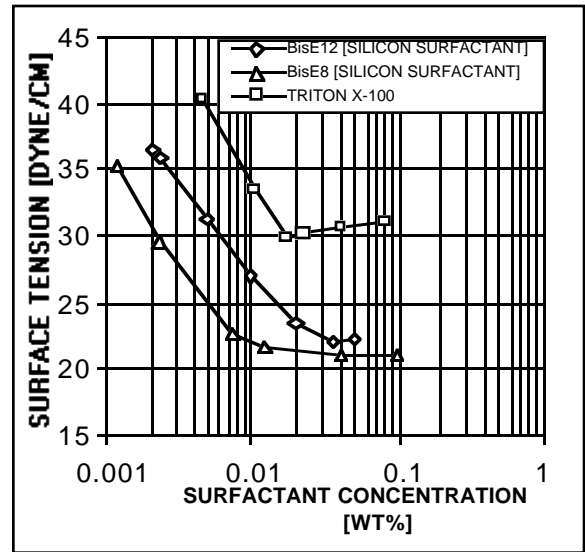


Figure 4 Relationship between surface tension and surfactant concentration with nonionic surfactants [BisE<sub>8</sub>, BisE<sub>12</sub> and Triton X-100] (Temp. = 22.8°C)

### 3. FOAMINESS.

The other important parameter used to characterize a foam is the *foaminess* or foam production capability of a foaming system. To evaluate foaminess the shaking test was used. Normally, for the shaking test, the foaminess parameter is the height of the foam produced after shaking during a given period of time and moderate agitation (Bikerman, 1973). The shaking test proposed here is more related to the maximum foam formation capability by shaking the sample very vigorously up to the condition where no change in



the total foam height is observed. The total foam height is recorded and the foaminess is calculated as follows:

$$\varepsilon_f = \frac{V_{foam} - V_{liquid}}{V_{foam}} \quad (4)$$

where:  $\varepsilon_f$ : foaminess [-]

$V_{foam}$ : volume of foam after shaking [cc]

$V_{liquid}$ : volume of liquid placed in the shaking tube [cc]

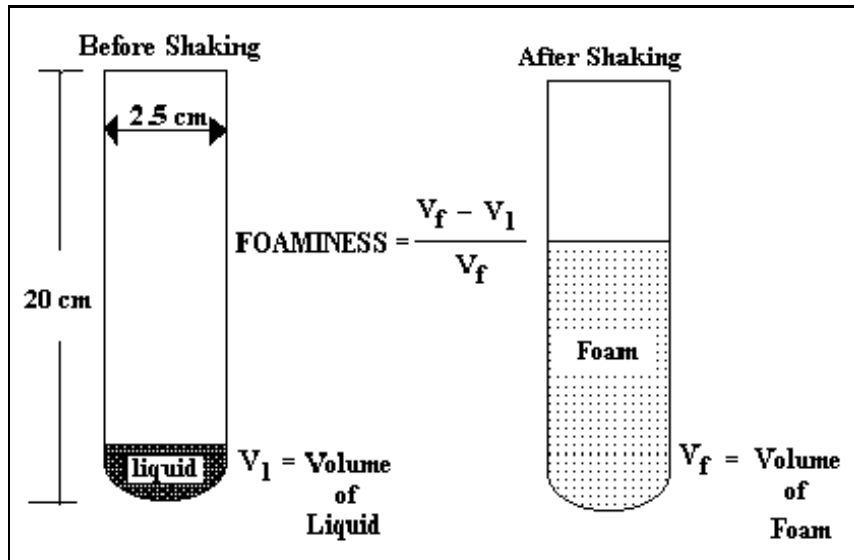


Figure 5 Cartoon of the shaking bottle to measure foaminess

This definition of foaminess and the methodology used is related to the maximum capacity of the foaming liquid to catch air. The foaminess so defined is the gas hold-up in the foam and can be related to the total area density of the foam using the following equation:

$$A = \frac{6V_{gas}}{d_b V_{liquid}} = \frac{6\varepsilon_f}{d_b (1 - \varepsilon_f)} \quad (5)$$

where:  $A$ : total area per unit volume of foaming liquid [cm<sup>2</sup>/cc]

$d_b$ : Sauter mean bubble diameter [cm]

$V_{gas}$ : volume of gas in the foam [cc]

The foaming measurements were conducted in a 2.5 cm diameter test tube of a volume of 100 cc (see Figure 5) in which either 10 gr, 15 gr or 20 gr of sample was

placed. The amount of sample depends on its foaminess. The total foam height must be less than 90% of the total height of the test tube to achieve full foam expansion. The experimental results show that the foaminess does not depend on the initial volume of the liquid sample. The experimental error was  $\pm 15\%$ . Figures 6a and 6b show foaminess of the different foaming systems evaluated as a function of surfactant concentration.

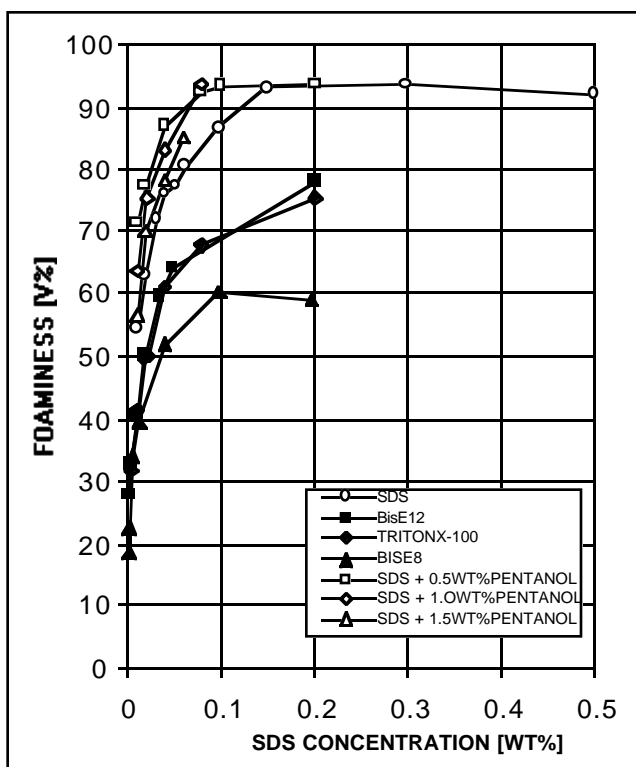


Figure 6a Foaminess as a function of surfactant concentration.

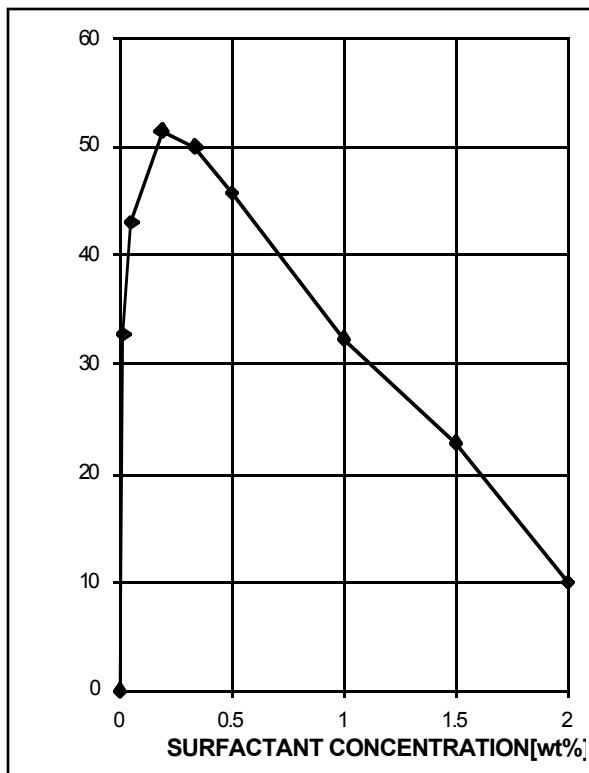


Figure 6b Foaminess of 1-Pentanol as a function of concentration.

Higher foaming is obtained with SDS and its mixtures with 1-pentanol when they are compared with the nonionic surfactants. Lower foaming is obtained in BisE<sub>8</sub>/water mixtures with a maximum value of 60v% which is also the system with the lowest surface tension of all the mixtures tested (Figure 6a). SDS and 0.5 wt% 1-Pentanol/SDS samples, have the maximum foaming and the highest surface tension.

This result shows that the foaminess is not determined by the equilibrium value of surface tension. All these surfactant mixtures show an increase of the foaminess when the surfactant concentration is increased up to a value above the CMC. The shape of these curves suggests that foam formation is related to the adsorption of the surfactant on the interface, resulting in the typical behavior of the Langmuir adsorption isotherm. The same type of behavior of foaminess as a function of concentration was reported by Malysa et al. (1991), where foaminess of fatty acid solutions was measured using a dynamic method (bubbling of air). They found that foaminess is related to the effective elasticity forces of foam films, due to the surface tension changes occurring during dilatational motion.

The foam film must be elastic in order to be able to withstand deformations without rupturing. If a surfactant stabilized film undergoes a sudden expansion, then the expanded portion of the film must have a lower density of surfactant per unit area than unexpanded portions. The depletion of surfactant increases the local surface tension and therefore increases the resistance to further expansions. If unchecked, further thinning would ultimately lead to film rupture. A local rise of the surface tension produces immediate contraction of the surface with liquid flow into the thin film from low tension into high tension regions. The transport of bulk liquid due to surface tension gradients is called the Marangoni effect and provides the resisting force to film thinning. This kind of resistance exists only until the surfactant adsorption equilibrium is reestablished in the film. The time taken to reach equilibrium depends on the film thickness, the surfactant adsorptivity and diffusivity at the surface and the bulk diffusivity. The restoration of equilibrium requires the movement of the surfactant along the interface and from the bulk regions of low to high surface tension, from non-depleted to surfactant depleted regions of the surface.

Many surfactant solutions give rise to dynamic surface tension behavior; time is required to establish the equilibrium surface tension. When the surface area is suddenly expanded, and diffusion of surfactant from the bulk is too low to restore equilibrium, the original adsorbed surfactant layer is either expanded or contracted due to the surface tension

gradients created. Marangoni forces are present and act in opposition to the disturbance. This fact explains why some surfactants that lower the surface tension do not stabilize foams (Adamson 1982); they are not able to restore the equilibrium fast enough after the expansion or contraction of the interface, in other words, they do not have enough surface elasticity. The foam films with adsorbed surface active materials provide the property that distinguishes foaming from non-foaming systems; the ability to resist excessive localized thinning of the film is the crucial property

The elasticity of foam could be measured by the Gibbs elasticity in the foam films

$$E_G = 2A \frac{d\sigma}{dA} \quad (6)$$

From the surface tension equation (2)  $d\sigma$  is given by:

$$d\sigma = - \frac{R_g T \Gamma_\infty dC}{(a + C)} \quad (7)$$

The total molar mass ( $M$ ) in the film is given by:

$$M = V_l C + 2A\Gamma \quad (8)$$

where  $C$  is the molar concentration in the bulk,  $V_l$  is volume of liquid in the film and  $\Gamma$  is the surface molar concentration. If we assume that the liquid volume is constant in the film ( $V_l = Ah$ ), then:

$$- \frac{dA}{A} = \frac{h dC}{2\Gamma} + \frac{d\Gamma}{\Gamma} \quad (9)$$

Equations (7) and (9) can be substituted into (2.1.2.13), and after simplifications using Langmuir adsorption isotherm [ $\Gamma = \Gamma_\infty C / (C + a)$ ] following Rosen (1967) we find that

$$E_G = 2A \frac{d\sigma}{dA} = \frac{4R_g T \Gamma_\infty^2 C}{(a + C)^2 (h + \frac{2\Gamma_\infty a}{(a + C)^2})} = \frac{4R_g T \Gamma^2}{C(h + \frac{2d\Gamma}{dC})} \quad (10)$$

If the surface is saturated, then  $d\Gamma / dC = 0$ , and

$$E_G = \frac{4R_g T \Gamma^2}{C h} = \frac{4R_g T \Gamma_\infty^2 C}{(a + C)^2 h} \quad (11)$$

which is zero when  $C=0$  and  $C=\infty$ . It follows then that  $E_G$  has a maximum for some  $C$  between 0 and  $\infty$ , already observed in the foaminess of the 1-Pentanol mixture (Figure 8).

A similar equation has been obtained by Andrew (1960), using a diffusion model to determine the dynamic rise of the surface tension. This parameter has been used also by Shah et al. (1985), Yang et al. (1985) as a criterion for the foaminess of alcohols and low molecular weight surfactants. Shah investigated the foaminess of  $C_2$  to  $C_4$  alcohols and found that the foaminess first increases with concentration up to a maximum and then decreases. The same behavior is obtained with a mixture of 1-Pentanol/water studied here (Figure 6b); an increase in 1-Pentanol results in decreasing foaminess beyond the maximum. This decrease of foaminess is superficially opposite to the results obtained with the other surfactants, in which an increase in concentration results in an increase in foaminess. We have not shown if a further increase in the surfactant concentration displayed in Figure 6a would lead to the same decreases observed in the 1-Pentanol/water system.

The mixture SDS/1-Pentanol shows a very peculiar behavior displayed in Figure 6a in which the foaminess of the mixture has a maximum for a finite concentration of 1-Pentanol at each fixed value of SDS concentration. Beyond the maximum any further increase in Pentanol concentration will result in a decrease of the foaminess of the mixture SDS/1-Pentanol. This behavior can be explained by an increase in the surface elasticity of the mixture at low 1-Pentanol concentration. At high 1-Pentanol concentration ( $>0.5$  wt%), the surface is almost saturated and any further increase in 1-Pentanol concentration will decrease the surface elasticity, resulting in a reduction of the foaminess of the mixture as shown in Figure 6b using 1-Pentanol alone. The work published by Lucassen-Reynders (1981) gives the same effects of surfactant concentration on Gibbs elasticity that

we have found. The Gibbs elasticity first increases and then decreases as the surfactant concentration is increased.

If  $\frac{d\Gamma}{dC} = \frac{\Gamma_{\infty}a}{(a+c)^2} \gg h$ , then equation (10) can be simplified to:

$$E_G = 2R_g T \Gamma_{\infty} \frac{C}{a} \quad (12)$$

This equation indicates that the  $E_G$  is proportional to the concentration, which can be related to foaminess at low concentrations as in Figures 5 and 6.

It may be assumed that for many surfactant systems  $dA/d\sigma = \alpha$  is very nearly constant as has been reported by Townsend et al (1986) for aqueous solutions of 1-butanol. For such systems the Gibbs elasticity is related to area by (6):

$$A = E_G / \alpha \quad (13)$$

This equation allows one to relate the foaminess  $\epsilon_f$  to concentration in a simple and useful form. After replacing  $A$  and  $E_G$  with equation (5) and (10) in (13), one finds that

$$\frac{6\epsilon_f}{d_b(1-\epsilon_f)} = E_G / \alpha = \frac{4R_g T \Gamma_{\infty}^2 C}{\alpha (a+C)^2 (h + \frac{2\Gamma_{\infty}a}{(a+C)^2})} \quad (14)$$

Generally,  $(h)$  the film thickness is a function of  $C$  and can be difficult to determine. However, one may assume that this is the film thickness when it is first formed, under the assumption that drainage is slow or that the times involved are much faster than drainage times. This is the case in a shaking bottle, because no significant liquid drainage has occurred immediately after shaking the sample. A useful theory has been given by Ivanov (1994) in which the concentration dependence of the initial thickness is essentially proportional to the reciprocal of the surface tension according to the relation

$$h = \frac{F}{4\pi\sigma} \quad (15)$$

where  $F$  is a constant force required to make a flattened sphere whose flat portion defines the film energetically more favorable than a sphere. In any case, we may and do treat  $F$  as a constant to be determined independent of  $C$ . Using the above mentioned formulation, then we have (14) in the form

$$\frac{\varepsilon_f}{(1-\varepsilon_f)} = \frac{2d_b R_g T \Gamma_\infty^2 C}{3\alpha (a+C)^2 \left( \frac{F}{4\pi\sigma} + \frac{2\Gamma_\infty a}{(a+C)^2} \right)} \quad (16)$$

Equation 16 is used to adjust the foaminess data obtained by the shaking method using the nonlinear regression software. The values of  $a$  and  $\Gamma_\infty$  are taken from the surface tension measurements. The adjustable parameters are  $F$  and  $d_b/\alpha$  where  $d_b$  is the average bubble diameter of the foam. The unit of concentration has been changed from wt% to mol/cc to keep dimensions consistent. Table 3 gives the adjusted parameters and the regression coefficient ( $R^2$ ) for each foaming system. Figures 7 and 8 show the comparison between experimental and calculated results. Very good agreement is evident considering that the surfactant samples are not 100% pure.

Higher discrepancies between the model and the experimental results are found in the low concentration range, especially with low foaminess surfactants where foaminess is higher than predicted. Under such conditions, the adsorption of the contaminants plays an important roll which is not considered in the model. The effect of the contaminants is smaller when the surfactant concentration  $\Gamma$  on the surface is large.

It is well known that alcohols have a maximum in foaminess at a given finite concentration. In Figure 8, we have plotted the foaminess against concentration of 1-Pentanol/water; the maximum foaminess predicted by the model is at 0.18 wt%. which is very near to 0.12 wt% reported by Bikerman (1973).

	Foaming System				
Constant	1-Pentanol water $\Gamma_{\infty}=6.35e-10$ mol/cm <sup>2</sup> a=1.53e-5 mol/cc	SDS water $\Gamma_{\infty}=7.13e-10$ mol/cm <sup>2</sup> a=6.91e-7 mol./cc	BisE <sub>12</sub> water $\Gamma_{\infty}=2.574e-10$ mol/cm <sup>2</sup> a=1.113e-10 mol./cc	BisE <sub>8</sub> water $\Gamma_{\infty}=2.7e-10$ mol/cm <sup>2</sup> a=7.67e-11 mol./cc	TritonX100 water $\Gamma_{\infty}=3.16e-10$ mol/cm <sup>2</sup> a=1.32e-9 mol./cc
$\frac{2d_b R_g T}{3\alpha}$	1.225e10	4.28e9	3.18e6	1.14e6	2.89e8
$\frac{F}{4\pi}$	0.00285	0.000193	3.21e-7	3.26e-7	1.753e-5
R <sup>2</sup>	0.99	0.99	0.97	0.85	0.94

Table 3 Adjusting parameters of foaminess equation 16

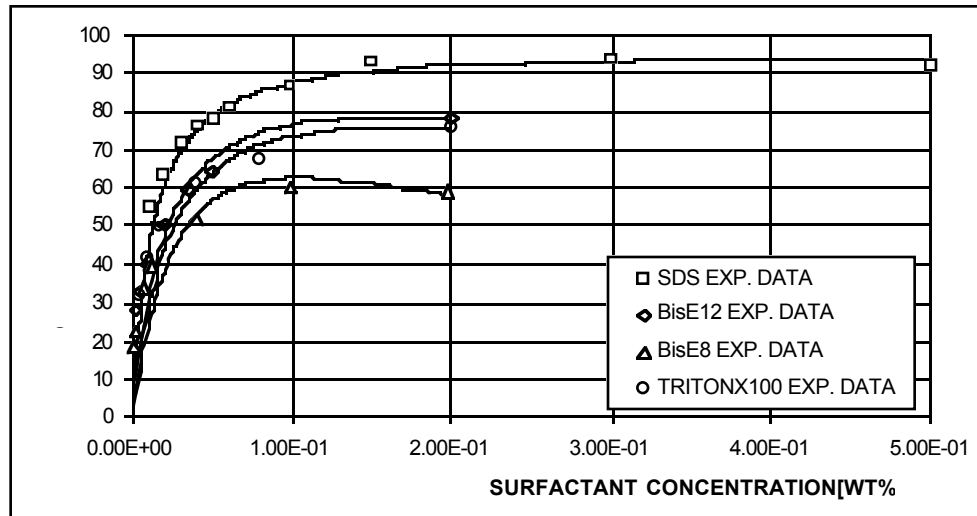


Figure 7 Foaminess results. Comparison of the model (16) and experiments

Another important result is that the foaminess is apparently not limited above the critical micelle concentration (CMC). All the surfactants we studied foams strongly even after the CMC. Similar results have been reported by Bikerman (1973), where for different alkylbenzene sulfonates molecules, the foam height after shaking increases for concentrations higher than the CMC.



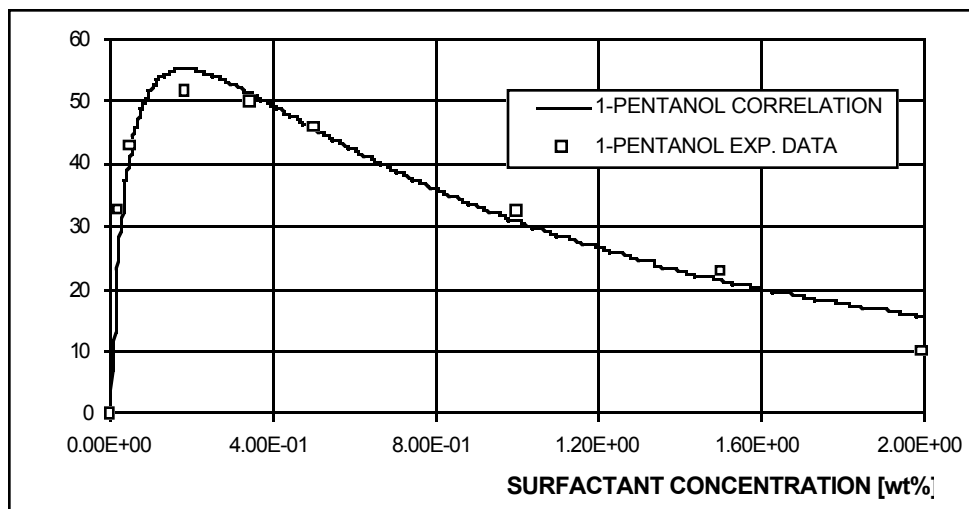


Figure 8 Foaming of 1-Pentanol/water. Comparison of model with experiments

A possible explanation of these apparent anomalies is that the equilibrium concentration  $\Gamma$  on the surface after the CMC is reached, is not obtained locally at many places in a foam undergoing severe mechanical deformation and the foam film is constantly under attack by the hydrodynamics conditions as in a shaking bottle or turbulent reactor. In any case the experimental evidence of the lack of relevance of the CMC is overwhelming.

The foaming of the mixture SDS/1-Pentanol/water cannot be predicted by equation (16) because the presence of two surfactants. Figure 6a suggests that the total foaming of the mixtures is the sum of the foaming contribution of the SDS and 1-Pentanol. Foaming first increases sharply when 0.5 wt% 1-Pentanol is added to the SDS solution; then the foaming decrease with a further increase in 1-Pentanol which is the same as was observed for the 1-Pentanol alone. The foaming increases with SDS to a maximum value of approx. 93v%; as was previously observed in solutions using SDS alone.

Considering these experimental observations, it is proposed that the foaming of the mixture SDS/1-Pentanol/water can be formed as a simple sum of the individual contributions of the Gibbs elasticity of each solution. Then (16) should be replaced by

$$A = (E_G^{SDS} + E_G^{C_5}) / \alpha \quad (17)$$

where  $E_G^{SDS}$  and  $E_G^{C_5}$  are the individual Gibbs elasticity of SDS and 1-Pentanol respectively. Therefore, equation (17) is replaced by

$$\frac{\varepsilon_f}{(1 - \varepsilon_f)} = \left( \frac{2d_b R_g T}{3\alpha} \right)^2 \sum_{i=1}^2 \frac{\Gamma_{\infty i}^2 C_i}{(a_i + C_i)^2 \left( \frac{F}{4\pi\sigma} + \frac{2\Gamma_{\infty i} a_i}{(a_i + C_i)^2} \right)} \quad (18)$$

where  $\sigma$  is the surface tension of the mixture

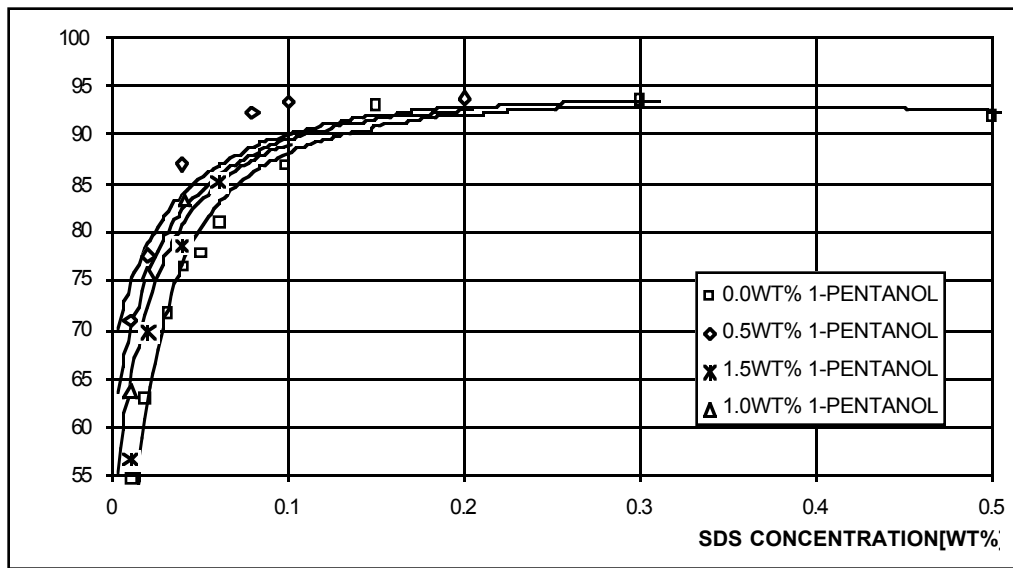


Figure 9 Foaminess results of SDS/1-Pentanol/water. Comparison between model and experiments.

Following the same procedure used previously, the parameters  $\alpha$  and  $F$  have been determined for the mixture SDS/1-Pentanol/water. Figure 9 shows satisfactory agreement between experiments and the theory (17). The regression coefficient for these experiments was  $R^2=0.95$  and the fitting parameters are  $2d_b R_g T / (3\alpha) = 4.65E-9$  and  $F / (4\pi) = 2.75E-4$ .

#### 4. CONCLUSIONS

It can be concluded that the foaminess of aqueous solutions of the surfactants used in the present experiments is strongly related to the capacity of the interface to absorb

surfactant. The foaminess which is a measurement of the area generated in a foam is proportional to the Gibbs elasticity in the foam film.

Considering that the samples employed were not pure, the proposed model based on Gibbs elasticity and two fitting parameters correlates the foaminess of the aqueous solutions of surfactants studied in all our experiments. Further work should be done to understand better the foaminess of the of mixtures with two or more surfactants

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## 6. REFERENCES

Adamson, A. W. (1982). Physical Chemistry of Surfaces (5th Edition). New York: Wiley.

Andrew S. P. (1960). Frothing in Two-Component Liquid Mixtures. International Symposium on Distillation. Instn. Chem. Engrs, 73-68.

Bikerman, J. J. (1973). Foams. New York: Springer-Verlag.

Ivanov, I. B. (1994) Interfaces Foams and Emulsions. Lecture Notes. Bulgaria: University of Sofia.

Lucassen-Reinders, E. H. (1981). In E. H. Lucassen-Reinders (Ed.), Anionic Surfactants Physical Chemistry of Surfactant Action. 173-216, Dekker, New York.

Malysa, K., R. Miller and K. Lunkenheimer (1991). Relationship between Foam Stability and Surface Elasticity Forces: Fatty Acids Solutions. Colloids and Surfaces, 53, 47-62.

Manegold, E. (1953). Schaum, Strassenbau, Chemie und Technick, 83 Heidelberg

Perry, R. H., and C. H. Chilton (1973). Chemical Engineers' Handbook (5th Edition). New York: McGraw-Hill.

Reid C. R. and Sherwood T. K. (1968). The Properties of Gases and Liquids. Their estimation and Correlation. New York: McGraw-Hill.

Ross, S. (1980). In Kirk-Othmer Encyclopedia of chemical Technology, 3rd edition. Wiley, New York, 11, 127-145

Ross, S., and I. D. Morrison (1983). On the allegeded Ideality of Szyszkowski-Langmuir adsorption. J. Col. Int. Sci., 91(1), 244.

Shah, Y. T. D. N. Smith, and J. A. Ruether (1985). On the Behavior of the Gas Phase in a Bubble Column with Ethanol-Water Mixtures. Ind. Eng. Chem. Process Des. Dev. 24, 1140-1148.

Townsend D. and Ross S. (1986). Dynamic Surface Tensions and Foaminess of Aqueous Solutions of 1-Butanol. Langmuir, 2, 288-292.

Yang, Y. M., and J. R. Maa (1985). Dynamic Surface Effect on Bubble Size and Froth Height. Journal of the Chin. I. Ch. E., 16(3), 283-288.