FOAMINESS AND FOAM STABILITY OF SURFACTANT SOLUTIONS

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Abstract

A combined pneumatic and mechanical foam generator was constructed and tested by sodium-dodecyl-sulfate and sodium-dodecylbenzene-sulfonate solutions. The foams could be divided into three classes according to the proportion of air incorporated into the foam. For better understanding the foaminess the dynamic surface tension of the solutions were measured under the same dilatational velocity as the beater products during foam forming.

Introduction

Foaminess is generally characterized by the volume of foam, that can be prepared from a given quantity of the liquid [1, 2]. The properties of a foam depend, in addition to the nature of the liquid, also on the degree of its dispersity and on the mode of dispersion. Therefore, foaminess indices are characteristic also to the method of foam forming beside the liquid tested. Foam beating is difficult to standardize, because foam forming can be undertaken for various purposes and with different methods. Methods of testing are generally modelling a given use.

The rate of foam forming may be taken as basis for the classification of foam forming. Three examples are given for the illustration of the possible difference between these rates.

In fire fighting foam generators the liquid is discharged from a nozzle and atomized by impingement. From the atomized liquid and air sucked in by the liquid jets, foam is formed in a short tube under froth flow in about 20–30 ms [3].

A tool often used for foam forming is the beater, which introduces under high-speed rotation bubbles into the liquid. According to the calculations of Prins, the freshly introduced high-pressure bubble is dilated to equilibrium size in 0.1–1 s [4].

Foam is formed when air is blown through a gas distributor sieve-plate into a foam-forming liquid. Bubbles formed at the bottom of the liquid layer rise to the top of the liquid, to form there first sphere foam, from which polyhedral foam is formed due to gradual drainage of the liquid. The development of polyhedral foam from bubble state through sphere foam takes several seconds.

The relative rate of surface dilatation at the formation of the bubble can be calculated from the microscopic model of foam forming [4]. The surfactant must stabilize the dilating surface. If the surfactant is adsorbed slowly, then the dilating surface will be "aquoid", and no foam films can develop.

The reciprocal of dilatation rate is proportional to the time needed on a liquid surface, freshly prepared then kept standing, to attain the same surface tension, by adsorption from the bulk of the liquid as by steady-state dilatation of the surface [5]. For this very reason, results of foaminess measurements will be suitably compared to the dynamic surface tension measured on a surface ageing or dilating in a way corresponding to the conditions of foam beating.

The comparison of different foaminess tests is hindered by uncertainty with respect to foam structure (bubble size, bubble distribution). It is conceivable that foams of identical volume are obtained from the same quantity of liquid by two different methods, but the structure of the foams is different. Therefore, the structure of foam generated in foaminess measurement must also be characterized. The rate of drainage from the foam can be most easily measured. This is, however, not an exact method because the results depend on the dimensions of the vessel, on the thickness of the foam layer, and moreover, drainage rate is influenced by at least two physical factors: the surface elasticity of the films and the size distribution of the bubbles. Surface elasticity is also connected with dynamic surface tension, however, from the aspect of foam stability the elasticity of the equilibrium film is essential [6].

Aims and modes of foam beating can be various. In certain cases only one part of the liquid is to be foamed (beer, soft drinks), in other cases foam must be formed with a small quantity of air (food-products), while it may happen that air as much as possible must be dispersed in the liquid (certain fire fighting foams), but avoiding foam can also be aimed (detergents for washing machines). In this paper a new method for the measuring of foaminess is described. In the development of the method none of the foam formings mentioned was modelled, but it was attempted to construct an equipment, suitable for the determination of the dispersion stabilizing power of surfactants. General requirements of fomainess test must necessarily include the following:

— characteristic time is well defined;

— the total quantity weighed in foams up;

— the foaminess of strongly foaming liquids can be measured.

Experimental

Measurement of foaminess and foam stability

Foam is beaten from the weighed-in solution with a single beating element of a Moulinex household robot (Model "Robot Marie"). The foam beating frame of about 6.5 cm height and 4.8 cm diameter is made of 2 metal wires of 1.5 mm diameter, perpendicular to each other. The foam is formed in a thermostated cylindrical vessel of 12 cm diameter and 15 cm height, having a bottom sloping towards the center, and fitted with a drainage tube.

The particularity of the process is that air of constant volumetric flow is introduced into the solution at the bottom. Air bubbled in forms initially large bubbles, films of large surface, because no air distributor was built into the conduit. The beater stretches out and breaks up these films. The speed of the beater, and through this the stretching and impingement rates of the films can be changed, that is, the strength of mechanical action is changeable.

Procedure is the following

Gas introduction (200 cm^3/min) is started, 25 cm^3 of the test solution is weighed into the foam beating vessel. The beater and a stop-watch are started. The foam is beaten until large-size—non-dispersed—air bubbles appear at the top of the foam. This time is marked with τ_f. Next, air introduction is stopped, and the foam is further beaten for a short time, to expel large air bubbles.

A graduated cylinder is placed under the discharge tube of the vessel, and the foam volume is measured with a levelling rod.

Beaten foam is not a stable formation, after stopping the beater the foam-liquid begins to drain downwards by the action of gravity, and when the films are saturated at the bottom of the foam with liquid [10], the liquid appears as a separate phase, and flows out from the vessel. The volume of this drainage is measured as a function of time. τ_{10} is the drainage time of 10% of the foam-forming liquid introduced, measured from the appearance of the first drop.

Calculations

From the above mentioned measuring data the specific volume of foam and the degree of "air utilization" were calculated. Specific volume is the ratio of foam volume (cm^3) and of the mass (g) of the liquid weighed in. The density of dilute aqueous solutions was taken as 1.0 g/cm^3, thus weighing in 25 cm^3 test solution $v = V_f/25$ cm^3/g.

Degree of air utilization

$\beta = V_f/V_{air}$. Air is introduced into the apparatus at a rate of 200 cm^3/min for a time τ_f, thus, the volume of total air introduced is $V_{air} = 200\ \tau_f/60\ cm^3$. Depending on the nature of the foaming substance

a) one part of the air introduced remains in the foam, while another part escapes, the degree of utilization is less than one ($\beta < 1$);

b) foam is formed only from air introduced, and air does not escape from the foam ($\beta = 1$);

c) external air is also beaten into the foam ($\beta > 1$).

Chemicals used in the experiments

Sodium-dodecyl-sulfate (NaDS), technical grade. Sodium-dodecyl-benzene-sulfonate (NaDBS), BDH Chemicals Ltd Poole (England), 80% of active substance, the rest sodium-sulfate. n-Octan-1-ol (C_8OL), BIOGAL, analytical grade. n-Dodecan-1-ol ($C_{12}OL$) of unknown origin. 4% C_{13-14} and 9% C_{10-11} homologous alcohols were detected by chromatographic analysis beside $C_{12}OL$.

Solutions were prepared under mild heating. Solutions containing alcohol were opalescent at the temperature of the experiments, at 25 °C.

The composition of the solution and beating speed were changed in the experiments. Composition of solutions are listed in Table 1. The first columns of Tables 2 and 3 giving measuring results refer to the series number of the Table 1.

Beating speed is characterized in the tables by the position of the toroidal transformer (adjustable from 0 to 100%), connected before the motor of the beater. 60% corresponds to a speed of 820 min^{-1}, 80% to 1120 min^{-1} and 100% to 1330 min^{-1}.

The estimated error of foam volume measurement is $\pm 25\ cm^3$, the estimated error of foam forming time ±15 s, and that of foam stability ±5 s.

Measuring results are summarized in Tables 2 and 3.

Table 1

Number of solution	Composition
1.	1.5 g/dm^3 sodium-dodecyl sulfate (NaDS) ($c \approx c_M$)
2.	1.5 g/dm^3 NaDS + 0.25 g/dm^3 n-octanol (C_8OL)
3.	1.5 g/dm^3 NaDS + 0.5 g/dm^3 C_8OL
4.	1.5 g/dm^3 NaDS + 0.5 g/dm^3 n-dodecanol ($C_{12}OL$)
5.	1.5 g/dm^3 NaDS + 0.25 g/dm^3 C_8OL + 0.25 g/dm^3 $C_{12}OL$
6.	1.2 g/dm^3 sodium-dodecylbenzol-sulfonate (NaDBS) ($c \approx c_m$)
7.	1.2 g/dm^3 NaBDS + 1 g/dm^3 (7.68 mmol/dm^3) C_8OL
8.	1.2 g/dm^3 NaDBS + 1.43 g/dm^3 (7.68 mmol/dm^3) $C_{12}OL$

Table 2

Foaminess and foam stability at 25 °C

Number of solution	Toroidal transformer %	τ_f [s]	τ_{10} [s]	V_f [cm^3]	V_{air} [cm^3]	β
1.	60	150	115	500	500	1.0
	80	125	105	400 – 500	420	1.0
	100	140	85	480 – 500	470	1.0
2.	60	170	67	650	570	1.1
	80	150	54	550	500	1.1
	100	170	65	500 – 550	570	0.9
3.	60	200	45	650	670	1.0
	80	175	65	600	580	1.0
	100	165	55	550 – 600	550	1.0
4.	60	175	105	270	580	0.5
	80	210	215	300	700	0.4
	100	235	345	300	780	0.4
5.	60	200	70	500 – 525	670	0.8
	80	150	65	450	500	0.9
	100	120	67	450 – 500	400	1.2
6.	60	140 – 150	90	500 – 550	470 – 500	1.1
	80	110	105	500	370	1.4
	100	95	105	450	320	1.4
7.	60.	150	68	500 – 550	500	1.1
	80	100	60	500	330	1.5
	100	90	60	500 – 550	300	1.8
8.	60	180 – 240	75	450	600 – 800	0.6
	80		90	350		
	100	330	90	350	1100	0.3

Table 3

Foaminess and foam stability at 40 °C

Number of solution	Toroidal transformer %	τ_f s	τ_{10} s	V_f cm^3	V_{air} cm^3	β	Ross–Miles, [Abe]
6.	60	158	45	650	530	1.2	270
	80	135	45 – 55	600 – 650	450	1.4	
	100	127	46	600	420	1.4	
7.	60	180	48	850	600	1.4	80
	80	175	37	800	580	1.4	
	100	130	40	750 – 800	430	1.8	
8.	60	187	50	600	620	1.0	190
	80	–	50	550	–	–	
	100	220	50 – 55	500 – 550	730	0.7	

Measurement of surface tension

Surface tension was measured at room temperature (24–25 °C) with the oscillating jet method [8]. The major axes of the elliptic orifice used for the generation of the liquid were 0.57 mm and 0.49 mm. Wavelength was read off from the ten times magnified image of the oscillating jet. The dynamic surface tension of solutions No. 1–4 is plotted as a function of the age of the surface in Fig. 1.

The dynamic surface tension of solution No. 5 was the same as that of No. 1, and therefore was not plotted. The surface tension of solutions Nos 6–8 at 40 °C was taken from the paper of Abe and Matsumura (Fig. 2).

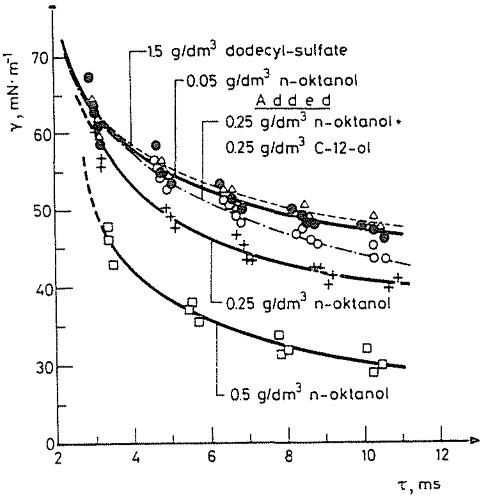

Fig. 1. Dynamic surface tension of NaDS solutions without (– – –) and with alkanols added at 25 °C

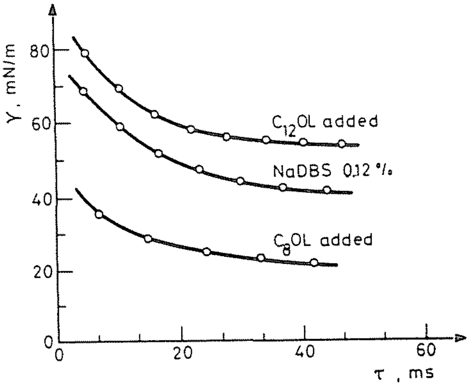

Fig. 2. Dynamic surface tension of NaDBS solutions without and with alkanols added at 40 °C after Abe and Matsumura [9]

The effect of the two alcohols on the foaminess (V_f) and foam stability (τ_{10}) of NaDS solutions

C_8OL increases foaminess, and decreases foam stability, the foam is soft, large bubbles formed at the end of foam beating rise easily and leave the foam. $C_{12}OL$ decreases foaminess, increases foam stability, the foam is hard, at the end of foam beating large bubbles are difficult to remove from the foam.

Varying beating speed the properties of soft foams hardly changed, while the stability of the hard (No. 4) foam considerably increased on increasing beating speed.

The foaminess of the mixture of the two alcohols (solution No. 5) is practically the same as that of the alcohol-free solution, that is, opposite effects balance each other. The foam stability of solution No. 5 is the same as that of solution No. 2, so that only the effect of C_8OL is reflected by stability.

The degree of air utilization is in the case of soft foams to a good approximation 1. In these cases the time of foam forming, τ_f, is proportional to the foam volume, foam beating from the solution of better foaminess needs more time only because the rate of gas introduction was kept constant. The conclusion suggests itself that the beating time of soft foams can be diminished by increasing gas introduction rate. In the forming of hard foam from solution 4 the degree of air utilization was less than 0.5, and decreased with increasing beating speed. It was observed during foam forming that the foam consists of very small bubbles, and the air introduced at the bottom of the apparatus is continuously and completely incorporated into foam. Nevertheless the fact that the degree of air utilization is as low as this, can be explained only by assuming that the beater bursts one part of the bubbles at the top of the foam. This conclusion is supported by the observation that the degree of air utilization diminishes with increasing beating speed.

The effect of the two alcohols on the foaminess and foam stability (τ_{10}) at 25 °C and at 40 °C

About the same quantity of foam can be formed from NaDBS solution as from NaDS solution, but its degree of air utilization is higher than one, so that NaDBS can be considered as a very well foaming substance (see solutions 1 and 6 in Table 3.). With increasing temperature the volume of foam formed from solution 6 increased, while β did not change. Additive C_8OL (solution 7) increased at 25 °C moderately, at 40 °C considerably foam volume, and increased also somewhat β.

The effect of additive $C_{12}OL$ can be best measured by the change of β: the foam is fragile, $\beta < 1$, the foam bursting effect diminishes with increasing temperature.

Foam stability, expressed with τ_{10}, was diminished by C_8OL, while $C_{12}OL$ slightly diminished at 25 °C and somewhat increased at 40 °C foam stability, as compared to pure NaDBS solution.

Discussion

In the foam beating vessel the foam practically does not move. (During operation the beater is slowly rotated, and thus, the frame always meets new foam portions.) The peripheral speed of the frame is about 300 cm/s. It is assumed for the calculation of dilatation rate that foam films adhering to the beater move together with it, further that behind the beater the foam stops, before the next frame gets there (Fig. 3). Along this section the relative dilatation rate is

$$\Theta = \frac{dv_r}{dr} \approx \frac{v_r}{s},$$

where s is the length of arch, along which the rate of the film increases from 0 to v_r. If this is taken as $s = 3$ cm, then $\Theta \approx 100\ s^{-1}$. According to the principle set forth in the introduction, the rate of the surface dilatation during foam beating corresponds to that of a surface ageing for a time $t = 0.01$ s. It can be said that the surface tension measured with the oscillating jet method in the time interval 5–10 ms corresponds to the surface tension of films dilated by a beater operated at a few m/s velocity and it can be attempted on this basis to compare foaming phenomena with dynamic surface tensions. C_8OL efficiently diminishes the surface tension of NaDS solution (Fig. 1), and increases foam volume. $C_{12}OL$ does not change dynamic surface tension, and diminishes foam volume, by making the films fragile. The two alcohols in the same solution neutralize each other: both surface tension and foaminess of solution 5 are identical to those of

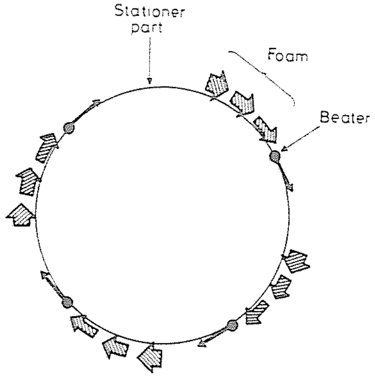

Fig. 3. Assumed foam velocity behind the beater

pure NaDS solution. Actions of opposite direction probably arise from the fact that the adsorption layer formed from NaDS and the alcohols is in one of the cases soft, while in the other rigid [7]. This is proved also by the fact that the stability (τ_{10}) of the foam containing $C_{12}OL$ (solution 4) is considerably higher, than that of the other solutions.

Surface tension measurements show that the diffusion rate of C_8OL is high, and it is incorporated into the adsorption layer within a very short time. It can be concluded from the increase in foaminess that C_8OL is adsorbed together with NaDS, because C_8OL in itself does not foam well. It is known that $C_{12}OL$ considerably diminishes the equilibrium surface tension of NaDS, while Fig. 1 shows that it does not change dynamic surface tension, so that $C_{12}OL$ is adsorbed slowly. Without $C_{12}OL$ the surface should be soft (see solution 1, $\beta = 1$). In spite of this, the foam of solution 4 can be broken up. This shows that during foam beating the foam ages, its films harden. When the beater reaches again the aged films, these are already unable to stretch, they burst. The other alcohol softens the aged films, which is manifested by the fact that in solution 5 $\beta \approx 1$, further that the τ_{10} stability of the foam is low. C_8OL increases the foaminess of NaDBS.

According to Ross–Miles' method foam is generated by a liquid jet impacting a liquid surface. Air bubbles mixed into the liquid are relatively slowly incorporated into the foam, the age of the films is at least 1–2 *s* on incorporation. It is supposed that the results of Ross–Miles's foaminess measurements cannot be compared to the dynamic surface tension obtained by oscillating jet measurements for surfaces of an age of a few hundredth seconds.

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