Factors Affecting Initial Foam Height in the Ross-Miles Foam Test

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Abstract

A study has been made of the relationship between initial foam height, H, as measured by the Ross-Miles test, and such factors as surfactant concentration, critical micelle concentration (CMC) of the solute, surface tension (γ) of the solution, surface area (A) of the foam, and the work involved in the production of the foam surface. The initial foam was remarkably constant in character for the systems studied and there was a linear relationship between H and A. For five of the six solutes used, the work of producing the foam surface fell within a narrow range at concentrations in the neighborhood of the CMC, indicating an inverse relationship between A and γ. For these solutes, $H \approx (1000/\gamma) - 3.6$. The maximum in H occurred in the neighborhood of the CMC.

Introduction

As part of an investigation of the parameters which determine foam formation in surfactant solutions, a study was undertaken of the factors which affect the initial foam height as determined by the Ross-Miles pour test method (1). The Ross-Miles method was selected for this purpose because it is one of the most widely-used tests for foaminess and has been adopted by the ASTM as a standard method (2). The method consists of running a standard volume of solution at a given temperature through a standard orifice onto a bed of the same solution in a cylinder at a fixed distance below the orifice and of determining the height of the foam produced thereby. Specifically, the present study is concerned with the relationship of the initial foam height to such factors as surfactant concentration, critical micelle concentration (CMC) of the surfactant, surface tension of the solution, surface area of the foam and the work involved in producing the foam surface.

In spite of its wide usage, the Ross-Miles test itself appears not to have been studied since the original work of Ross and Miles. The literature makes no mention of such fundamental information as the size of the bubbles produced, their reproducibility with similar solutions or their variation with change in concentration or structure of the solute. Since it is logical to assume that the initial foam height must in some manner be related to the work required to produce the foam, and since an estimate of the work necessary to produce the surface of the foam can only be obtained from a knowledge of the bubble sizes in the foam, the present study includes an investigation of that aspect of the phenomenon.

The minimum work (W_s) required to produce a foam surface from a solution is equal to the product of the total surface area (A) of the foam produced, and the surface tension (γ) of the solution from which it is produced, which yields:

$$W_s = \gamma A. \qquad [1]$$

To evaluate A, an exact knowledge of the size distribution of the bubbles in the foam is required. In order to obtain this information, the foam produced was photographed and enlarged prints or projections of the photographs were analyzed visually.

Preliminary tests showed that the shape of the bubbles in the foam was spherical for the first few minutes after its formation. Therefore, under these conditions, the following expression is obtained:

$$A = \sum_{i,j} 4\pi\, r_i^2\, n_j \qquad [2]$$

where n is the number of bubbles of radius, r, in the foam. Furthermore, these tests showed that in all the systems studied, the foam consisted of two distinct sections: (a) a small portion (section B) about 14 mm high, at the very bottom of the foam, which contained tiny bubbles of 0.1–1.8 mm diameter and (b) a major, upper portion (section U) comprising the remainder of the foam, which contained bubbles from 0.5–4.0 mm in diameter. Only rarely were bubbles larger than 4 mm encountered, and these were confined almost exclusively to the very top of the foam.

Experimental Procedures

Materials Used

$C_{14}H_{29}SO_3K$ and $C_{16}H_{33}SO_3K$ were prepared and purified by the procedure described previously (3). $C_{12}H_{25}SO_3Na$ (purissima grade) was purchased from Aldrich Chemical Company. $C_{12}H_{25}SO_4Na$ was obtained through the courtesy of M. B. Epstein, of the Colgate-Palmolive Company, Jersey City, N.J. $C_{16}H_{33}SO_4Na$ and Na Me α-sulfopalmitate were obtained through the courtesy of A. J. Stirton, Eastern Regional Research Laboratory, U.S. Dept. of Agriculture, Philadelphia, Pa.

TABLE I
Average Bubble Radius of Section U of the Foam

Solute	Concentration (M)	Conc./ CMC[a]	Average Bubble Radius (mm)[b]
$C_{12}H_{25}SO_3Na$	1.50×10^{-2}	1.15	0.5_5
	1.00×10^{-2}	0.77	0.5_8
	0.80×10^{-2}	0.61	0.5_9
	0.40×10^{-2}	0.31	0.6_4
$C_{12}K_{25}SO_4Na$	1.18×10^{-2}	1.17	0.6_5
	0.788×10^{-3}	0.77	0.5_3
$C_{14}H_{29}SO_3K$	3.50×10^{-3}	1.17	0.5_3
	3.00×10^{-3}	1.00	0.5_9
	2.50×10^{-3}	0.83	0.6_3
$C_{16}H_{33}SO_3K$	1.00×10^{-3}	1.11	0.5_7
	0.75×10^{-3}	0.83	0.5_8
	0.50×10^{-3}	0.56	0.6_2
	0.25×10^{-3}	0.28	0.7_0
$C_{16}H_{33}SO_4Na$	0.828×10^{-3}	1.27	0.5_5
	0.828×10^{-3} +.01 M NaCl		0.5_4
	0.621×10^{-3}	0.96	0.5_7
	0.414×10^{-3}	0.64	0.5_3
	0.207×10^{-3}	0.31	0.5_1
	0.207×10^{-3} +.01 M NaCl		0.5_6
Na Me α-Sulfopalmitate	4.00×10^{-3}	$\cong 2$	0.5_5
	2.00×10^{-3}	$\cong 1$	0.5_7

[a] CMCs at 60 C.
[b] Subscripts indicate doubtful figures.

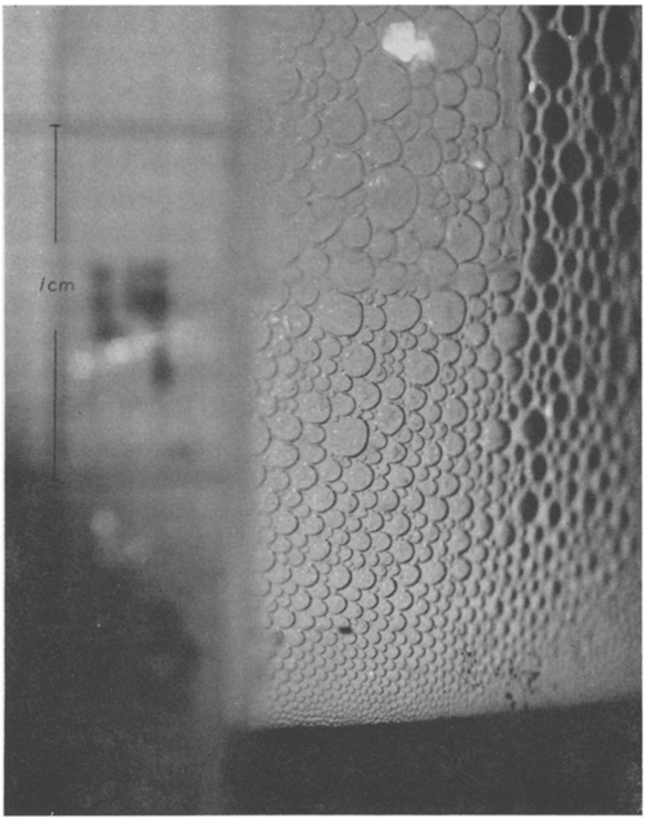

Fig. 1. Photograph of Section B of the foam.

Foaming Technique

The apparatus and procedure used were those of ASTM method D1173-53 (2), with the exception that the assembly used in the ASTM method at the top of the column to hold the pipet in place was replaced by ordinary flask clamps, and positioning of the pipet was accomplished with a spirit level. The foam cylinder used had an internal diameter of 4.89 ± 0.01 cm at 60 C. All tests were conducted at 60 ± 0.5 C. Glassware was cleaned by immersion in hot 1:9 HNO_3–H_2SO_4 mixture for 30 min, followed by rinsing with distilled water, redistilled acetone, and finally with quartz-distilled water. The foam cylinder was cleaned by passing the hot HNO_3–H_2SO_4 mixture down the walls, followed by copious rinsing with distilled water, and finally with quartz-distilled water.

The initial foam height was taken as the height of the foam 60 sec after the last drop of solution had drained from the pipet. This interval was selected because rapid drainage of liquid from the foam had ceased by this time.

TABLE II
Distribution of Bubble Sizes in Section B

Radius (mm)	Per cent
0.05	24
0.10	20
0.15	18
0.20	12
0.25 0.30	14
0.35 0.40	7
0.45 0.50	4
0.55 0.60	2
0.65— 0.90	0.5

TABLE III
Distribution of Bubble Sizes in Section U

Radius, mm	Per cent
0.25	30
0.50	40
0.75	12
1.00	10
1.25	6
1.50	1.5
1.75	0.5

Average bubble radius: 0.57 mm.

Five or six runs were made with each solution; initial foam heights tabulated are averages of values from these runs.

Surface Tension Measurements at 60 C

All surface-tension measurements were made by the Wilhelmy plate technique described previously (3). To minimize evaporation, the dishes containing the solutions were covered with the two halves of a split watch glass, one of which contained a V-shaped notch through which the string holding the platinum plate passed when measurements were being taken.

Average Bubble Radius in Section U of the Foam

The average bubble radius in this major portion of the foam was obtained by counting the number of bubbles per 2 cm vertically at six different positions along the wall of the foam column. Data are given in Table I.

Calculation of Surface Areas of Foam in Sections B and U from Photographs

Detailed analysis of the distribution of bubble sizes in the foam column was carried out in four cases for section B and in eight cases for section U. Photographs of the foam were taken after 1 min, on 35 mm film. A telephoto lens was used for the small bubble portion (section B).

Photographs were either enlarged and printed (Fig. 1) or projected onto a screen, and the distribution of bubble sizes was determined by inspection. The number of bubbles in each size range for small vertical sections of the portion of the film photographed was counted and the cumulative surface area $\sum_{i,j} 4\pi r_i^2 n_j$, and the cumulative volume corresponding to those bubbles, $\sum_{i,j} 4/3\pi r_i^3 n_j$, were calculated. The simplifying assumption was made that the photographed portion was typical of the foam as a whole at that height in the foam column.

The surface area of any small vertical section of the foam of height, h, is expressed as follows:

$$\frac{\pi R^2 h}{\sum_{i,j} 4/3\pi r_i^3 n_j} \times \sum_{i,j} 4\pi r_i^2 n_j$$

where R is the internal radius of the foam column.

In section B, the bubbles had radii less than 1 mm and a radius range of ±0.05 mm was used in determining n. The distribution of bubble sizes varied considerably with vertical position in the section, the percentage of very small bubbles decreasing rapidly with height in the foam column. The approximate overall distribution of bubble sizes in the 14 mm of this section is shown in Table II.

In section U, the bubbles had radii less than 2 mm (except for a few bubbles at the very top of the

TABLE IV
Surface Area of Section B (14 mm) From Photographs

Solute	Concentration (M)	Conc./CMC	Total surface area (10^3 cm^2)[a]
$C_{12}H_{25}SO_3Na$	1.00×10^{-2}	0.77	2.9_4
$C_{14}H_{29}SO_3K$	2.50×10^{-3}	0.93	3.1_2
$C_{16}H_{33}SO_3K$	0.50×10^{-3}	0.56	3.0_1
$C_{16}H_{33}SO_4Na$	0.83×10^{-3}	1.27	3.0_0

[a] Subscripts indicate doubtful figures.

TABLE V
Total Surface Areas and Average Surface Area/cm of Foam Height in Section U, From Photographs

Solute	Concentration (M)	Height of T (cm)[a]	Total surface area (10^3 cm^2)[a]	Average surface area/cm foam height (10^2 cm^2/cm)[a]
$C_{12}H_{25}SO_3Na$	1.00×10^{-2}	$19._4$	11.5_7	5.9_5
$C_{16}H_{33}SO_3K$	1.00×10^{-3}	$21._9$	13.7_2	6.2_7
	0.75×10^{-3}	$21._7$	13.2_8	6.1_1
	0.50×10^{-3}	$19._2$	10.9_7	5.7_0
	0.25×10^{-3}	$15._6$	8.9_3	5.7_1
$C_{16}H_{33}SO_4Na$	0.828×10^{-3}	$20._6$	12.3_8	6.0_5
	0.621×10^{-3}	$19._4$	12.1_7	6.2_6
Na Me α-sulfopalmitate	4.00×10^{-3}	$19._2$	11.6_2	6.0_5

[a] Subscripts indicate doubtful figures.

foam) and a radius range of ±0.25 mm was used in determining n. In contrast to the situation in section B, the distribution of bubble sizes in this section of the foam varied only slightly with vertical position. The approximate overall distribution of bubble sizes in this section is shown in Table III.

The total surface area of the foam in both these sections was obtained by a summation of the surface areas of the individual small vertical sections of the foam over the entire height of the foam in that section. For section U, in addition, the average surface per centimeter of foam height was calculated by dividing the total surface area of this section of the foam by the height of this section. Results are given in Tables IV and V.

Discussion

Bubble Sizes and Surface Areas of the Foam

The data obtained indicate that, at least for the systems studied, the initial foam produced in the Ross-Miles test is remarkably constant in character with variation in the nature or concentration of the surface-active solute. The relatively narrow variation in the average bubble radius (Table I), obtained by relatively crude measurements, is confirmed by the detailed analyses of the enlarged photographs of the foam. The total surface area of the small bubble section (lower 14 mm) of the foam (Table IV) and the average surface area per vertical centimeter of the upper, major section of the foam (Table V) show surprisingly small variation with change in the chain length or concentration of the solute. Moreover, the average bubble radius of 0.57 mm determined from the size distribution of the bubbles in that section of the foam is in good agreement with the values in Table I.

The small variation in the total surface area of section B and in the surface area per vertical centimeter of foam in section U permits estimation of the total surface area, A, of the foam merely from the initial foam height. Using a value of 3.0×10^3 cm^2 for the surface area of section B and a value of 6.0×10^2 cm^2 per vertical centimeter of the foam in section U,

$$A = 600(H - 1.4) + 3{,}000$$
$$= 600(H + 3.6) \qquad [3]$$

where H = initial foam height, in centimeters. Values of A, calculated in this manner, are listed in Table VI for the solutions investigated.

Work of Producing the Foam Surface, W_s

Using these values of A and the surface tensions of the solutions at the same temperature (60 C), values of W_s, the minimum work required to produce the foam surface, were calculated using Equation 1, above. These values are given in Table VI.

For five of the six solutes investigated, the values of W_s fall within 10% of 6.0×10^5 ergs at concentrations in the neighborhood of the CMC. This value represents 3% of the total potential energy lost by the test solution in dropping from the orifice onto the solution bed below and implies that there is a maximum amount of that potential energy which can be transformed into surface free energy. The reason for the low values of W_s obtained with the $C_{16}H_{33}SO_4Na$ solutions may be a trace of surface-active impurity in that solute, as evidenced by the lower surface tensions of solutions of that solute at concentrations in the vicinity of its CMC as compared to those of the sulfonate of equal chain length, $C_{16}H_{33}SO_3K$. In addition to the possible effect of this presumed impurity upon initial foam heights, the lower values of γ of necessity yield smaller values of the γA product, W_s.

TABLE VI
Calculated and Observed Parameters of Solutions Tested

Solute	Conc./CMC	H, cm (obs.)[a]	A[b], 10^3 cm^2 (calc.)[a]	γ(60 C)[a]	W_s(10^5 ergs)[a]	H, cm (calc.)[a]
$C_{12}H_{25}SO_3Na$	1.15	$21._0$	$14._8$	$38._2$	$5._7$	$22._6$
	0.77	$20._8$	$14._6$ ($14._5$)	$42._5$	$6._2$	$20._0$
	0.61	$20._0$	$14._2$	$45._3$	$6._4$	$18._5$
	0.31	$16._5$	$12._1$	$55._2$	$6._7$	$14._5$
$C_{12}H_{25}SO_4Na$	1.19	$20._4$	$14._4$	$38._7$	$5._6$	$22._2$
	0.77	$18._3$	$13._1$	$42._1$	$5._5$	$20._1$
	0.40	$14._9$	$11._1$	$52._1$	$5._8$	$15._6$
$C_{14}H_{29}SO_3K$	1.17	$21._4$	$15._0$	$35._9$	$5._4$	$24._2$
	1.00	$21._7$	$15._2$	$36._1$	$5._5$	$24._1$
	0.83	$21._1$	$14._8$	$40._9$	$6._1$	$20._9$
	0.58	$20._4$	$14._4$	$43._4$	$6._2$	$19._5$
$C_{16}H_{33}SO_3K$	1.11	$23._3$	$16._1$ ($16._7$)	$36._1$	$5._8$	$24._1$
	0.83	$23._1$	$16._0$ ($16._3$)	$38._2$	$6._1$	$22._6$
	0.56	$20._6$	$14._5$ ($14._0$)	$44._6$	$6._5$	$18._8$
	0.28	$17._0$	$12._4$ ($11._9$)	$52._3$	$6._5$	$15._5$
$C_{16}H_{33}SO_4Na$	1.27	$22._0$	$15._4$ ($15._4$)	$32._0$	$4._9$	……
	0.96	$20._8$	$14._6$ ($15._2$)	$34._5$	$5._0$	……
	0.64	$12._9$	$9._9$	$38._6$	$3._8$	……
	0.31	$11._1$	$8._8$	$54._5$	$4._8$	……
Na Me α-Sulfopalmitate	≅2	$20._6$	$14._5$ ($14._6$)	$39._5$	$5._7$	$21._7$
	≅1	$20._5$	$14._5$	$39._9$	$5._8$	$21._5$

[a] Subscripts indicate doubtful figures.
[b] Values in parentheses are observed values from photographs.

TABLE VII
Effect of NaCl Addition on Initial Foam Height

Solute	Conc./CMC	NaCl Conc. (M)	Initial foam height (cm)[a]	γ(60 C)[a]	W_s 10^5 ergs (calculated from Equation 4)[a]
$C_{16}H_{33}SO_4Na$	1.27	0	$22._0$	$32._0$	$4._9$
	1.27	0.01	$21._8$	$31._8$	$4._8$
$C_{16}H_{33}SO_4Na$	0.31	0	$11._1$	$54._5$	$4._8$
	0.31	0.01	$19._4$	$33._6$	$4._6$

[a] Subscripts indicate doubtful figures.

The relatively narrow range of the values of W_s in the neighborhood of the CMC implies that A is inversely proportional to γ in this concentration range. Since, as shown above, A is a function (Equation [3]) of the initial foam height, H, we can write an expression as follows

$$W_s = \gamma A = 600\gamma(H + 3.6) = \text{constant} \qquad [4]$$

For five of the six solutes investigated, the value of W_s is approximately 6×10^5, from which:

$$H \approx (1000/\gamma) - 3.6. \qquad [5]$$

Values of H, calculated by use of this expression, are listed in Table VI. In view of the simplifying assumptions made and the limitations in the accuracy of the measurements, the agreement between calculated and observed values of H is considered satisfactory.

In order to test this dependance of H on γ, a small amount of NaCl was added to two solutions whose initial foam heights had previously been determined. It is well known that the addition of a small amount of electrolyte to a solution of an ionic surfactant whose concentration is below its critical micelle concentration will result in a decrease in the surface tension of that solution, whereas there will be little or no decrease in the surface tension if the solution is above its CMC. The results of these experiments are given in Table VII. They confirm the dependance of H upon γ in that the solution whose surface tension was decreased by the addition of NaCl showed an increased foam height, while the solution whose tension remained essentially unchanged, upon the addition, showed no change in initial foam height. The close agreement of the values of W_s is additional evidence for the validity of Equation 4 as a quantitative expression of this dependancy.

Initial Foam Height and Surfactant Concentration

The dependance of H upon γ accounts for much of the data on foaming by use of this test reported in the literature (4–7). The Ross-Miles test, as commonly used, measures foam heights of solutions at a given weight concentration, usually 0.25%. However, it has been shown by Gray et al. (7) that foam height in this test increases to a maximum with concentration and Goette (8), using other foam-producing methods, has found a relationship between foam properties and the critical micelle concentration of the solute. No attempt, however, appears to have been made to correlate the onset of this maximum in the foam height in the Ross-Miles test with the CMC. It is apparent from the data in Table VI, where initial foam heights are listed versus conc./CMC at 60 C, that the onset of this maximum in the foam height is in the neighborhood of the CMC. Initial foam height increases rapidly with increase in concentration of the solute until the CMC is reached and then remains relatively constant. In view of the dependance of H upon γ shown above, this variation in the foam height with concentration is readily understandable as a reflection of the well-known rapid decrease in γ with increase in concentration of the solute to a minimum value when the CMC is reached. Thus, although the members of a homologous series of surfactants may have very different foam heights when compared at the same weight concentration, when they are compared at concentrations close to the CMC, their foam heights fall within a narrow range reflecting the difference in surface tensions of these solutions.

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