On the Nature of Foam. I. Stability of the Foam Produced by the Aqueous Solutions of Alcohols and Acids.

By Tunetaka SASAKI.

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The phenomena of the foam formation have been studied for long time by numerous investigators referring, for example, to the brewing and soap industries, the process of flotation of minerals, priming of boiler water, and other practical cases, as well as on the theoretical standpoints. Attemps have been made to explain the mechanism of foaming.

The relation between the foaming and the surface tension which was considered to be the most important factor for the foam formation was studied by Ramsden,(1) Metcalf,(2) Freundlich,(3) Bartsch,(4) and others. They concluded that the foams are stabilised when there exist the difference in concentrations of the solute between the surface and the bulk of solution, the depression of the surface tension by adsorption, and the film formation. Ostwald and Steiner,(5) however, showed that there are stable foam systems of large surface tension, aqueous humic acid solution, for example, and that the lowering of the surface tension even breaks the foam. They pointed out that some other factors than the surface tension must be introduced to explain the mechanism of the foam formation. Further, the following factors are generally considered to affect the foam formation, and many reports have been published concerning them: orientation,(6) hydration,(6)(7) adsorption,(8) rigidity(1)(9)(10) or structural viscosity,(5) electrical charge,(5)(10) gelation,(1)(4) and evaporation(6)(11) of films or surface layers respectively. None of these factors in itself shows the simple relation to the foam formation. Accordingly,

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(1) W. Ramsden, *Z. physik. Chem.*, **47** (1904), 336.
(2) M. V. Metcalf, *Z. physik. Chem.*, **52** (1905), 1.
(3) H. Freundlich, "Kapillarchemie," 1091, (1924).
(4) O. Bartsch, *Kolloid-Beihefte*, **20** (1925), 1; *Kolloid-Z.*, **38** (1926), 177.
(5) Wo. Ostwald and A. Steiner, *Kolloid-Z.*, **36** (1925), 342.
(6) D. Talmud and S. Suchowolskaja, *Z. physik. Chem.*, **154** (1931), 277.
(7) R. H. Bogue, *J. Am. Chem. Soc.*, **44** (1922), 1343.
(8) C. W. Foulk, *J. Ind. Eng. Chem.*, **21** (1929), 815; **23** (1931), 1283.
(9) O. Rohde, *Ann. Physik*, **19** (1906), 935.
(10) P. Rehbinder and E. Wenström, *Kolloid-Z.*, **53** (1930), 145.
(11) H. A. Neville and T. H. Hazlehurst, *J. Phys. Chem.*, **41** (1937), 545.

it is desirable, prior to the discussion of this problem, to analyse the phenomena of the foam formation precisely.

The most important property characterising the foam formation is the stability of foam. It can also be considered as the durability or the life time of foam. The other factor sometimes adopted but not so distinct is the foam producing power. This factor was vaguely considered by Bartsch(4) and lately explained by Foulk(8) to be the possibility of film formation when two surfaces in one liquid approaches each other, and was called "Balanced-layer theory". The following examples are given to explain the above consideration. When we shake the dilute aqueous solutions of saponin and acetic acid, following differences are observed. The foam of saponin solution is more stable but less foamy than that of acetic acid solution. Further, beer and champagne are both foamy but the foam of the former is more stable than that of the later. The foam formation, therefore, may be considered to consist of two factors,(12) namely the stability of foam and the foam producing power, but the latter factor is rather indistinct and quantitative measurements are only possible for the former, so it is desirable that we can explain the mechanism of the foam formation without considering the latter factor.

The measurement of the stability of foam is the important method for the study of the foam formation and is carried out by several means. For example, a vessel containing the solution under investigation is shaken and the volume or the height of foam produced and the duration of its existence are measured.(4) Sometimes the current of air or other gas of constant pressure and volume is passed through the solution instead of the shaking.(8)(13) The former method is mainly applicable to the solution producing a stable foam such as the aqueous solution of saponin or soap. Other factors than the stability of foam may affect the results obtained by the former method. The latter method, however, gives quantities only proportional to the stability of foam, and is mainly applicable to the measurement of the unstable foam such as produced in the aqueous fatty acid or alcohol solution.

The present paper describes the measurements of the stabilities of foams of aqueous solutions of fatty acids and alcohols.

Apparatus and Measurement. The apparatus employed in the present experiment has been constructed as shown in Fig. 1. In this figure, A is a bottle containing glass wool and calcium oxide, B the foam produc-

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(12) Practically bubble size must be considered still more.

(13) E. L. Lederer, *Z. angew. Chem.*, **47** (1934), 119.

ing tube, C paraffin-oil flow meter, D an empty bottle, E an air current controller consisting of a rubber tube and a screw cock, F an empty flask with a cock for the air leak. The foam producing tube B consists of a glass tube of 1.1 cm. in diameter carrying a porous plate at the bottom.

The measurement is carried out as follows: At first the inner tube of B is carefully cleaned by dipping in boiling water and steaming with water vapour, and dried by passing dry air through it. Then the constant volume (up to the height of 4.5 cm. from the bottom) of liquid for measurement is introduced in the tube by means of water jet pump connected at G, and the air current controller is properly adjusted, so as to obtain the condition in which the flow meter indicates a constant velocity of air current. Then, the air current, passing through the porous plate at the bottom of B, produces bubbles in the liquid, which go up and accumulate to make foam on the surface of the liquid. The height of the foam zone thus produced is measured by the scale attached to the tube. The air current of one atmospheric pressure is introduced into the tube at the velocity of 33.2 c.c./min. or 35 cm./min. in linear velocity, and 3 minutes are passed from the start to attain this velocity. Care is taken not to pass the air current too vigorously, otherwise the border between the bubble and foam zone becomes obscure.

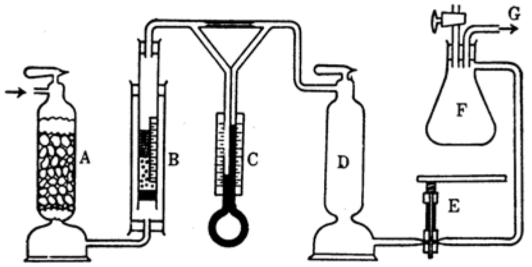


Fig. 1.

Now, we denote with H the height of foam at the stationary state, v the velocity of a bubble ascending the foam zone, and S the stability of the bubble in the foam zone. Then we obtain the following relation:

$$S \cdot v = H \,, \qquad \text{or} \qquad S = \frac{1}{v} \cdot H \,.$$

Therefore, if we assume v to be constant, the stability is proportional to the foam height, and we can determine the relative stability of foam if we measure the foam height at the constant velocity of the air current. The foam height has often been measured under the air current of constant static pressure,⁽⁸⁾ but such a method, of course, cannot be used under the present experimental conditions. Thus, the diagrams are obtained by plotting the foam height against the time. The foam height at the time zero can be obtained by extrapolation which enables to cancel the disturbances produced by the evaporation or other factors becoming distinctive in the course of time. Some of the examples of the results obtained by the above method for aqueous solution of *n*-butyl alcohol are shown in Table 1 and Fig. 2.

Table 1. *n*-Butyl alcohol. (0.5378 mol/liter).

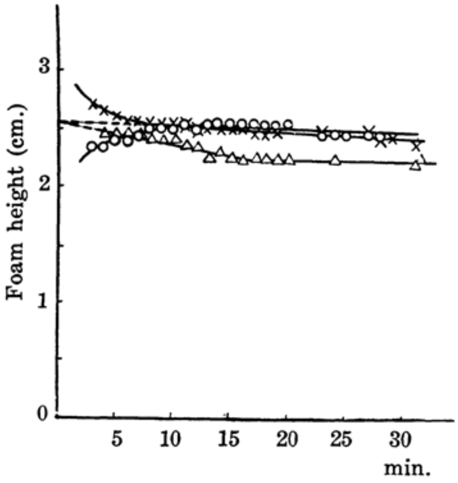
Time (minute)	Height of foam (cm.)			Time (minute)	Height of foam (cm.)		
	1	2	3		1	2	3
3	2.35	2.70	2.35	17	2.25	2.45	2.55
4	2.45	2.65	2.35	18	2.25	2.45	2.55
5	2.45	2.60	2.40	19	2.25	2.45	2.55
6	2.45	2.55	2.40	20	2.25	—	2.55
7	2.45	2.55	2.45	21	—	—	—
8	2.40	2.55	2.50	22	—	—	—
9	2.40	2.55	2.50	23	—	2.45	2.45
10	2.40	2.55	2.50	24	2.25	—	2.45
11	2.35	2.55	2.55	25	—	—	2.45
12	2.35	2.50	2.50	26	—	—	—
13	2.25	2.50	2.55	27	—	2.45	2.45
14	2.35	2.50	2.55	28	—	2.40	—
15	2.25	2.50	2.55	29	—	2.40	—
16	2.25	2.50	2.55	30	—	—	—
				31	2.20	2.35	—

In most cases, diagrams of straight lines are obtained differing in its direction even in the measurements under the same conditions, but the extrapolation of the lines to time zero generally gives the same value of H. There often occur the cases where the foam becomes very high at the beginning of the measurement, or it shows the irregular height with the time, but the stationary state is usually attained after such stages. In the worst case, about twenty minutes are necessary to attain the stationary state.

Prior to the principal experiments, the measurement of the foam height H is carried out at varying velocities of air current and at varying concentrations for the aqueous solution of *n*-hexyl alcohol in order to examine the relation $S{\cdot}v = H$. The results obtained are shown in Fig. 3.

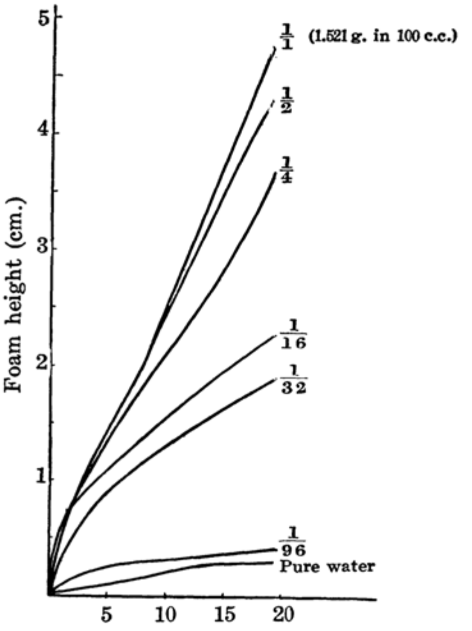
It is concluded from this experiment, that the following equation expresses more closely the relation between v and H.

$$S{\cdot}v = H - a\,.$$



n-Butyl alcohol.

Fig. 2.



Hexyl alcohol.

Fig. 3.

The correction term a varies with the concentration of the solution, and at slow velocity and optimum concentration, it takes a marked value, but at high speeds as are adopted in this experiment, the value is very small compared with H. So we shall consider the height H to be proportional to the stability S in the present experiment.

Experimental Results. The experimental results are shown in the diagrams (Fig. 4.–Fig. 11.). These diagrams are obtained by plotting the foam heights at the constant velocity of air current against the concentrations of the aqueous solutions of alcohols and fatty acids. At the same time, surface tensions are measured by Du Nöuy's apparatus and plotted against the concentrations. Table 2 shows the numerical data for the solution of *n*-butyl alcohol.

The following conclusions are obtained from the above experiments: (1) The stabilities of foams produced in the pure substances are zero or very small as can be seen from Figs. 4–11 or Table 3.

Measured heights of the foams never exceeded that of one bubble. This agrees with the known fact that the pure liquids do not foam on

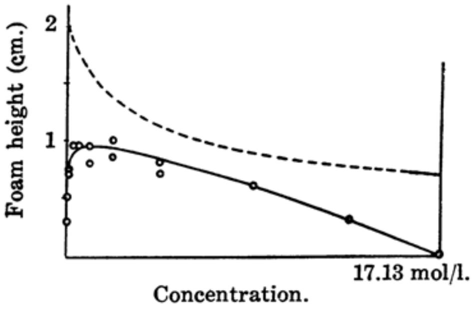


Fig. 4. Ethyl alcohol.

Fig. 4 – Fig. 11.

1: Surface tension of the pure alcohol or acid.
2: Foam height of heterogeneous system.
3: Foam height of the pure alcohol or acid.

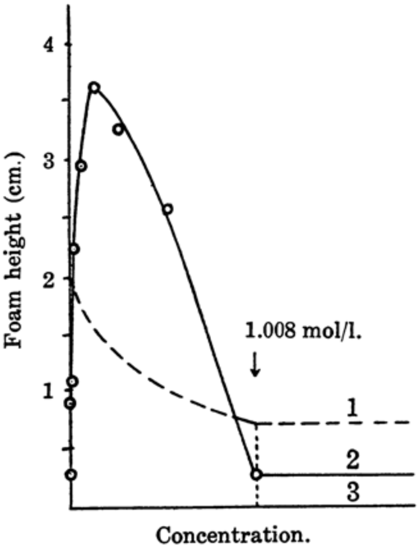


Fig. 5. *n*-Butyl alcohol.

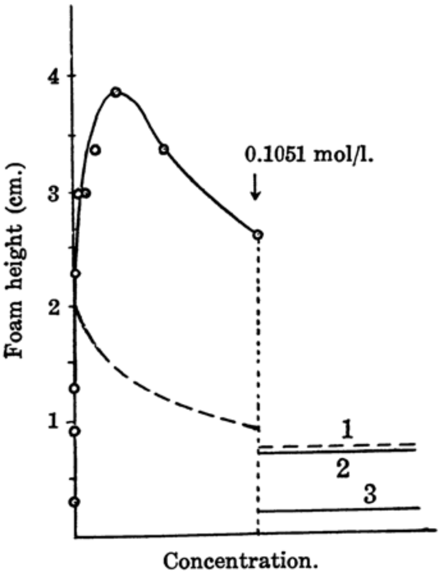


Fig. 6. *n*-Amyl alcohol.

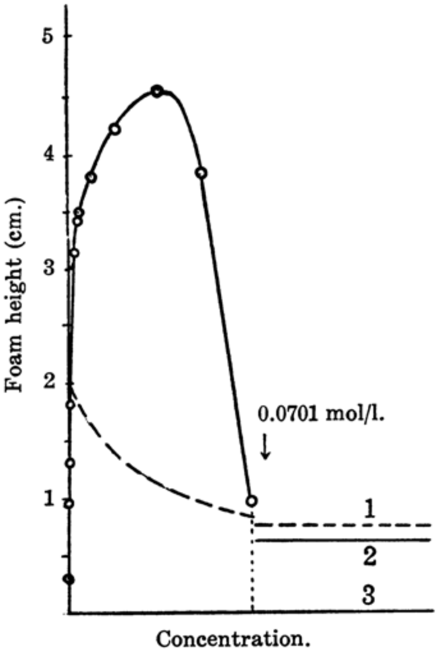


Fig. 7. *n*-Hexyl alcohol.

Table 2. *n*-Butyl alcohol.

Concentration (mol/liter)	Height of foam (cm.)	Surface tension (relative)
0	0.30	1.000
0.0021	0.90	0.998
0.0042	1.10	0.996
0.0084	—	0.981
0.0168	2.24	0.958
0.0336	—	0.908
0.0672	2.96	0.837
0.1345	3.60	0.743
0.2689	3.24	0.632
0.5378	2.54	0.504
1.0080*	0.25	0.372
Heterog. system	0.25	—
Pure butyl alcohol	0.00	0.371

* Saturated solution.

Table 3.

Substance	Height of foam (cm.)	Surface tension (relative)
Water	0.30	1.000
Ethyl alc.	0.00	0.342
n-Butyl alc.	0.00	0.371
n-Amyl alc.	0.20	0.376
n-Hexyl alc.	0.00	0.390
n-Octyl alc.	0.00	0.395
n-Decyl alc.	0.15	0.409
Formic acid	0.00	0.559
Acetic acid	0.00	0.393

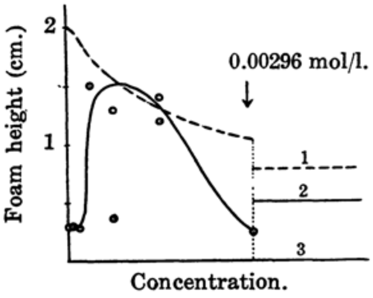


Fig. 8. *n*-Octyl alcohol.

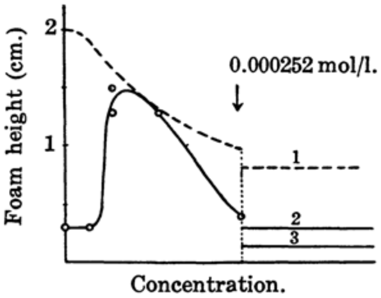


Fig. 9. *n*-Decyl alcohol.

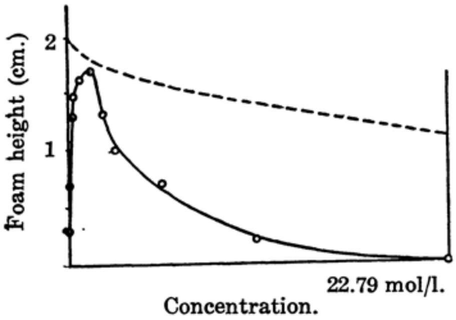


Fig. 10. Formic acid.

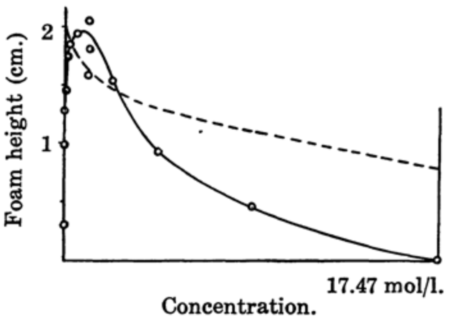


Fig. 11. Acetic acid.

agitation,⁽⁸⁾ and is likely to indicate the existence of some relationship between the foam formation and the adsorption. It can also be seen from Table 3 that the absolute magnitude of the surface tension is not the determining factor for the foam formation.

(2) In the aqueous solutions of alcohols and fatty acids, the diagrams of stability and concentration show one marked maximum usually at the concentration where the surface tension falls rapidly with the dilution, namely in the region of the dilute solution. The measurement of stabilities for the solutions of *n*-octyl alcohol shows a remarkable irregularity.

Table 4.

Substance	Conc. of maximum stability		Foam height at maximum stability (cm.)	Surface tension	
	mol/liter	C/C_0*		relative	absolute (dyne/cm.)
Ethyl alc.	1.07	2/32	0.95	0.79	56.9
n-Butyl alc.	0.126	4/32	3.60	0.75	54.0
n-Amyl alc.	0.0131	8/32	3.85	0.81	58.3
n-Hexyl alc.	0.0350	16/32	4.56	0.68	48.6
n-Octyl alc.	0.00105	9/32	1.50	0.75	54.0
n-Decyl alc.	0.0000733	11/32	1.50	0.77	55.1
Formic acid	1.26	1.8/32	1.70	0.90	64.8
Acetic acid	0.819	1.5/32	1.95	0.85	61.2

* Concentration expressed by the fraction of saturated concentration.

In Table 4, the values of surface tension of alcohols in the solutions of maximum stability of foam range from 48 to 59 dynes/cm. They do not always agree with the results obtained by Bartsch⁽⁴⁾ in which the maximum stabilities occurred in the solution of the surface tension near 61 dynes/cm. Although the surface tension shows no regularity, there can be seen a certain relationship between the concentration of maximum stability and the number of carbon atoms in the molecule of solute. Namely, the concentration of the maximum stability expressed by mols per liter decreases and that expressed by the fraction of the saturated concentration increases with increasing number of carbon atoms as are shown in Table 4 or in Fig. 12.⁽¹⁴⁾

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(14) Logarithm of the solubility of fatty alcohol in water measured in this experiment is linear to the number of carbon atoms in its molecule.

(3) The foam height at maximum stability increases with increasing number of carbon atoms from ethyl to *n*-hexyl alcohol while decreases with further increase of carbon atom which is shown in Fig. 13. Thus, *n*-hexyl alcohol gives the maximum foam stability. The result may be compared with that obtained by Bartsch(4) who pointed out that iso-amyl alcohol has the maximum foam stability.

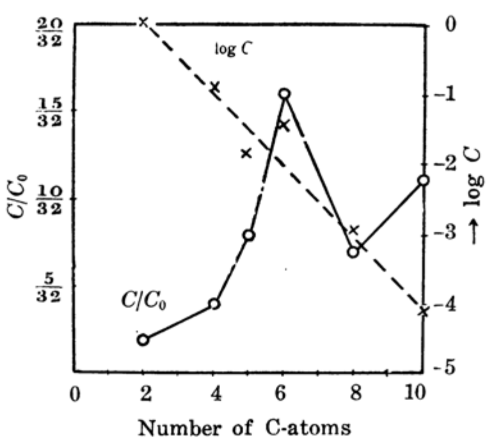
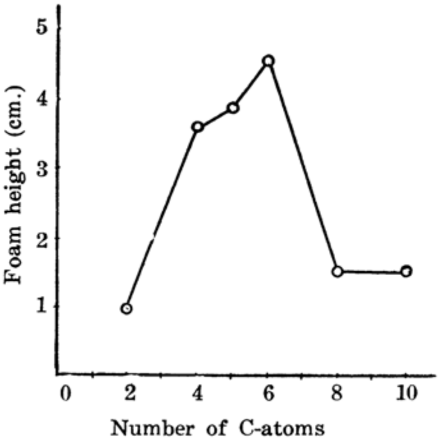


Fig. 12.



Aliphatic alcohols.

Fig. 13.

(4) In the heterogeneous systems of water and *n*-butyl alcohol or the higher homologue which has limited solubility in water, the stability of foam is very small, excepting the case of *n*-amyl alcohol as is shown in Table 5.

Table 5.

Substance	Foam height of heterogeneous system (cm.)
n-Butyl alcohol	0.25
n-Amyl alcohol	0.7
n-Hexyl alcohol	0.6
n-Octyl alcohol	0.5
n-Decyl alcohol	0.3

In the heterogeneous systems of water and surface active or polar substances such as fatty alcohols or acids, the stabilities of foams are usually zero or very small, the explanation of which being given in the preceding note.(15) Namely, the heterogeneous films containing drops of the excess component break the foam produced. In practice, hexyl alcohol or octyl alcohol which is

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(15) Sasaki, this Bulletin, **11** (1936), 797.

used as the antifoam is the polar or surface active and hardly soluble substance and favours to produce such heterogeneous films.

On the other hand, there are many cases in which the foams are stabilized even in the heterogeneous systems. The examples are those which consist of an aqueous phase and various non-polar liquid phases of low surface tension, such as benzene or hexane. For instance, foams of the aqueous solution of acetic acid are killed by the addition of hexyl or octyl alcohol in excess, while stabilized by the addition of benzene or hexane in moderate excess.

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Summary.

(1) An apparatus for the measurement of the stability of foam has been described and the stability is measured by the height of the foam produced by the air current of a constant velocity.

(2) The relation between the velocity of the air current v and the height H of the foam produced was examined and the equation $S \cdot v = H - a$ has been obtained, in which S is the stability of foam and a a constant. The value a is negligible compared with H under the conditions of the present experiments.

(3) The measurements of the stabilities were carried out for the aqueous solutions of alcohols and fatty acids, from which several conclusions have been obtained.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.