On the Nature of Foam. VII.[1] Foam Formation of Mixed Aqueous Solution of Saponin and Ethyl Alcohol.

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It is a problem of fundamental importance for the study of foam phenomena to clear the mechanism of its formation.

It has already been pointed out that it is reasonable to assume two factors to explain the mechanism of foam formation, namely, the stability of foam and foam producing power(2). Though we cannot yet at present define these two quantities satisfactorily, they are briefly explained as follows. In ordinary cases, the stability of foam has relatively close relationship to a life of foam, for example, an aqueous solution of saponin or soap gives fairly stable foam on shaking which sometimes shows a life of several days, while in the case of solutions of alcohols or fatty acids, foam is unstable and short-living which last for only about thirty seconds. Foam is stabilized chiefly by the existence of plasticity or rigidity in foam film(3), of saponin for example. Foam producing power, on the other hand, means the degree of easiness with which foam is produced. This factor is rather pronounced in solutions of alcohols and fatty acids. In practice, measurements carried out in properly dilute solutions of alcohol (butyl alcohol for example) and saponin shows that the foam volume(4) of the former is larger although its life is shorter than those of the latter. Foam producing power is favoured by low surface tension and perhaps low viscosity, as in the case of aqueous solutions of surface active substances.

Now, there occurs a case where a considerable degree of foam formation is observed in dilute mixed solution of saponin and ethyl alcohol, even when foam cannot be produced in solutions which contain these solutes separately but in the same concentrations as in the mixed solution. Such a foam formation of mixed solution can be explained as the results of combined effects of stability due to saponin and foam producing power due to ethyl alcohol, either of which alone is not sufficient for the foam formation as in the cases of separate solutions.

Present paper describes the results and explanations of these and some other related phenomena.

Apparatus and Measurement. Measurements of the degree of foam formation were carried out with such mixed aqueous solutions of saponin

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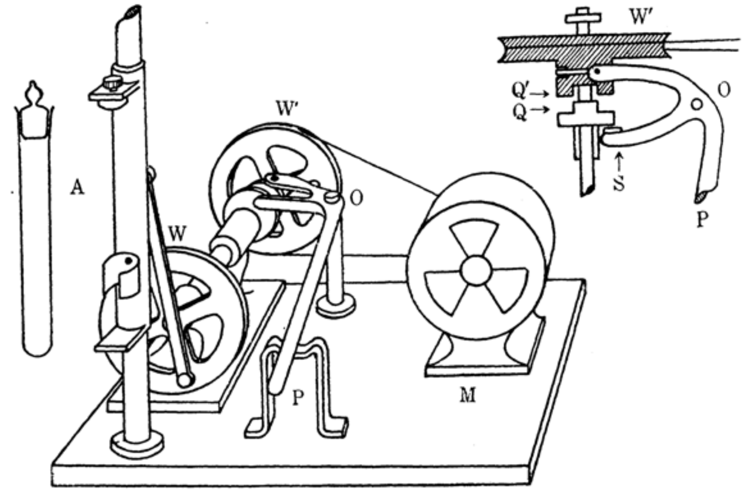
(1) The former reports are the followings: Sasaki, this Bulletin, **11** (1936), 797; **13**(1938), 517; **13**(1938), 669; **14**(1939), 3; **14**(1939), 63; **14**(1939), 107; **14** (1939), 250.

(2) Sasaki, this Bulletin, **13** (1938), 517.

(3) Wilson and Ries, Colloid Symposium Monograph, **1** (1923), 145; Talmud, Suchowolskaja and Lubman, *Z. physik. Chem.*, A **151** (1930), 401.

(4) Volume of foam measured immediately after the stop of shaking is relatively in close relation to foam producing power.

and ethyl alcohol as they contain both solutes in a constant and varying concentration respectively.



P —handle, rotatable around the point O.
W —wheel with a crank.
W'—wheel, connected to P and be able to slide on axis of W.
S —brake acting on W.
M —induction motor.
A —test tube and its supporter.
Q, Q'—projections belonging to W and W' respectively and acting as joint between them.

Fig. 1.

Foam was produced by shaking apparatus as shown in Fig. 1. In this Figure, by moving handle P rightwards, wheel W' shifts towards W to which it is connected by means of joint Q and Q'. Then, the test tube A containing liquid is made to vibrate by setting the motor M in motion. The vibration is interrupted by leftward movement of the handle P with resulting action of brake S upon W.

Conditions of measurement were the same as in the former report(5), namely, 10 c.c. of solution for measurement is introduced in a well stoppered test tube (1.5 cm. in diameter and 15 cm. in length) and is shaken 50 times for 10 seconds with an amplitude of 12 cm. After shaking, following quantities are measured.

H_0, height of foam zone (in cm.) produced immediately after the stop of shaking.

H_5, height of foam zone in five minutes after shaking, in the case required.

L, Life of foam (in second).

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(5) Sasaki this Bulletin, **13** (1938), 669.

Results of Measurement. The results of measurement were shown in Tables 1, 2 and Figs. 2–5. Concentration of saponin was in one case 0.009085 g./l. as in Table 1, Fig. 2 and Fig. 3, (system A) while in another case, it was 0.001820 g./l. as in Table 2, Fig. 4 and Fig. 5. (system B). These conditions were adopted as the critical concentration, namely, the former concentration of saponin in water corresponds to the heighest possible dilution at which solution still foams, while at latter concentration, aqueous solution of saponin foams no more. In Figs. 2–5, H_0, H_5 and L are quantities referring to the mixed solution, and H_0' and L' are those referring to the solution of alcohol without saponin, for comparison.

Table 1.

Conc. of saponin (g./l.)	Conc. of alcohol (mol/l.)	H_0 (cm.)	H_5 (cm.)	L
0.009085	0	0.8	0	65.5 sec.
0.009085	0.0005143	0.7	0	25.5 sec.
0.009085	0.002572	0.8	0.5	>5 min.
0.009085	0.005143	1.2	0.8	>5 min.
0.009085	0.02571	2.3	1.7	>5 min.
0.009085	0.05143	3.1	2.2	>5 min.
0.009085	0.2571	4.8	3.4	ca. 2 hour
0.009085	0.5143	4.7	3.5	>5 min.
0.009085	0.7713	3.9	1.3	>5 min.
0.009085	1.029	4.4	0	17.6 sec.
0 009085	1.543	4.6	0	10.0 sec.
0.009085	17.13	0	0	0 sec.

Table 2.

Conc. of saponin (g./l.)	Conc. of alcohol (mol/l.)	H_0 (cm.)	L (sec.)	H_0' (cm.)	L' (sec.)
0.001820	0	0	0	0	0
0.001820	0.0005143	0.5	0	0	0
0.001820	0.002572	0.6	11.8	0	0
0.001820	0.005143	0.8	54.3	ca. 0.5	0
0.001820	0.02571	1.4	57.0	1	2.0
0.001820	0.05143	2.0	86.0	1.2	5.0
0.001820	0.2571	3.4	59.0	1.9	7.8
—	0.5143	—	—	1.8	7.6
0.001820	0.7714	3.2	12.0	—	—
—	1.029	—	—	3.1	7.5
0.001820	1.543	2.7	5.5	2.7	7.1
—	5.143	—	—	1.7	2
0.001820	17.13	0	0	0	0

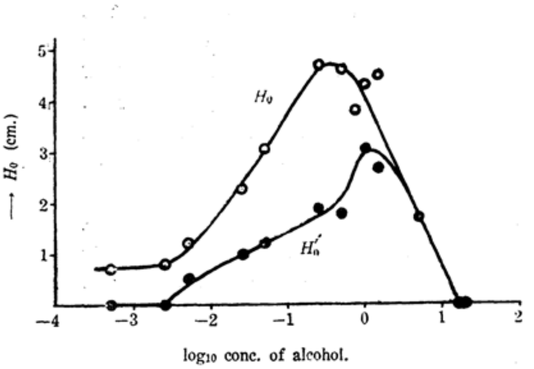

Fig. 2. Mixed solution of saponin and alcohol.
saponin = 0.009085 g./l

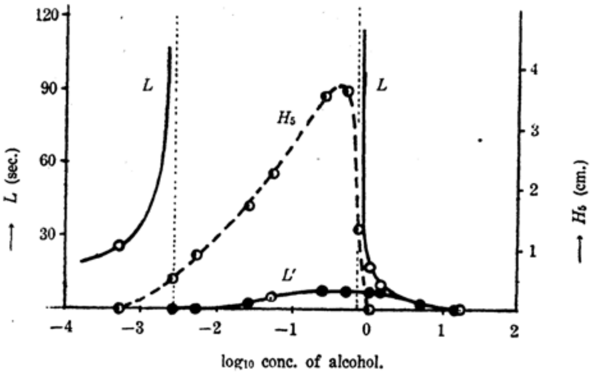

Fig. 3. Mixed solution of saponin and alcohol.
saponin = 0.009085 g./l.

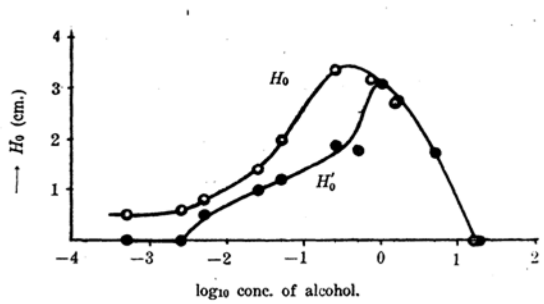

Fig. 4. Mixed solution of saponin and alcohol.
saponin = 0.001820 g./l.

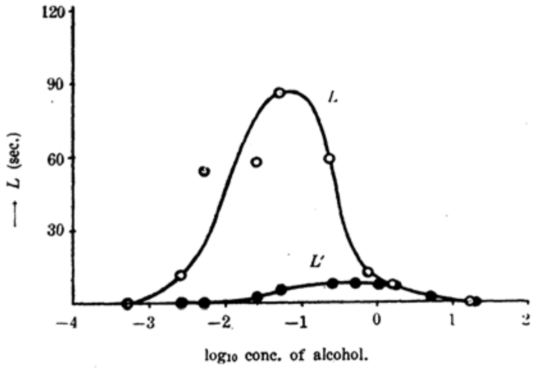

Fig. 5. Mixed solution of saponin and alcohol.
saponin = 0.001820 g./l.

It can be seen in Figs. 2 and 4, that diagrams of $H_0 \sim$ conc. and $H_0' \sim$ conc. as a whole are analogous to each other. The foam height of mixed solution shows a magnitude which can be expected from that of corresponding alcohol solution, that is, the foam height of mixed solution is mainly determined by alcohol, and saponin shows only a little or no effect at all. When we observe, however, the relation between life of foam and concentration of alcohol in mixed solution as shown in Figs. 3 and 5, we find the followings. In the system A, foam life of saponin solution is increased in length from 65 seconds to more than 5 minutes by the addition of merely about 0.0026 mol/l. of alcohol. In the optimum case, foam lasting for about two hours can be obtained by the addition of 0.2571 mol/l. of alcohol. Foam life of solution containing alcohol alone, is also very small compared with that of mixed solutions as shown in Fig. 3. When foam life amounts to more than five minutes, the result of its measurement becomes uncertain. In such a case, foam height in five minutes after shaking is indicated instead of its life, for convenience. Foam life of the mixed solution is remarkably reduced by the addition of alcohol in excess (over concentration of 0.77 mol/l.). In the system B, the phenomena are similar, though not so marked as in the system A. In this system, a mixed solution containing both 0.001820 g./l. of saponin and 0.005143 mol/l. of alcohol shows a foam life of 54 seconds, while solutions containing these amounts of solutes separately do not foam at all. ($L=0$). As a whole, foam life of saponin solution is fairly increased in length by the addition of alcohol within the region of concentration covering over from 0.0026 mol/l. to 0.77 mol/l. for both systems.

Discussion. Now, the explanation of the above phenomena is attempted.

(1) On the stand point of foam formation, saponin solution is marked for its stabilizing action, while foam producing power is characteristic for alcohol solution as described in the introduction of this paper. It is, therefore, reasonable to assume that the foam height of mixed solution which is perhaps closely related to foam producing power, is mainly determined by the properties of alcohol, and is not affected by the presence of saponin, because of its little foam producing power in such a dilution as in the present experiment. The remarkable increase in length of foam life of mixed solution, on the other hand, can be explained either as the stabilizing action of saponin for the foam formation of alcohol solution, or inversely, as the foam producing action of alcohol for saponin solution, that is, the action of alcohol to increase the degree of dispersion of saponin foam. Thus, the life of foam measured under these conditions is considered to be affected both by the foam producing and stabilizing action of solutes. In the region of such remarkable foam formation of the mixed solution, these two actions are attributed to saponin and alcohol respectively.

(2) In the region of mixed solutions, however, where the concentration of alcohol exceeds certain limit(6), above two actions are exclusively determined by alcohol. This is especially pronounced in the case of the system B as shown in Figs. 4 and 5. Here, the life and height of foam measured in a mixed solution containing alcohol in concentration of more than 1.029 mol/l, shows the same value as in the corresponding alcohol solution without saponin. In such a case, properties of liquid films consisting foam are considered to be the same for both solutions, practically. The similar phenomena can also be observed in the system A, though a little less pronounced. These may be explained either from the preferential adsorption of alcohol in surface of foam film with an exclusion of sapoin, or from dehydrating action of alcohol for saponin particles in foam film. Concerning to the former explanation, the possibility may be suggested for observing a state of preferential adsorption of a solute from a mixed solution by the measurement of properties exhibited by liquid films, such as the life and height of foam. As to the latter explanation, it is interesting, in this connection, to describe further the properties of foam as a disperse system.

(3) As a disperse system, foam can be considered to be a suspension or emulsion, the disperse phase of which is replaced by air or by the other gases, and so it is a kind of hydrosol in wider sence. Foam can, therefore, be divided also into two types, that is, hydrophilic and hydro-

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(6) 1.543 mol/l. and 1.029 mol/l. for systems A and B respectively.

pholic foams(7), quite analogous to the hydrophilic and hydrophobic sols in the case of aqueous suspension(8). Hydrophilic foam is relatively stable as produced in saponin or soap solution, and is insensitive for electrolyte. Hydrophobic foam, on the other hand, is unstable like that of alcohol or fatty acid solution, and is sensitive for electrolyte. Hydrophilic foam can also be rendered unstable by the addition of alcohol with resulting dehydration of foam film, just as in the case of hydrophilic sol. This is the case described in (2). But, just reverse to this phenomenon, we have also noticed the increase in length of the life of saponin foam by the addition of relatively small amount of alcohol as shown in the preceding section. We cannot, however, find the similar instance in aqueous suspension at all. This lack of analogy between foam and suspension is explained as follows.

In the case of aqueous suspension, effects of alcohol are measured in a system already dispersed preceding to the addition of alcohol, while in the case of foam, the same effects are observed in a system which is dispersed by shaking or by other means after the addition of alcohol. Therefore, in latter case, effects of alcohol during the process of dispersion and consequently upon the foam produced, must be considered in addition to those in the case of aqueous suspension. Accordingly, the phenomena can be explained if we take into account of the fact that the decrease in surface tension of saponin solution and some other effects which are produced by the addition of alcohol, favour a high degree of dispersion(9).

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Summary.

(1) The foam formation of mixed aqueous solution containing saponin in a constant amount and ethyl alcohol in varying concentration was studied. Life of the foam produced in aqueous solutions of saponin (concentrations being 0.009085 g./l. and 0.001820 g./l.) is remarkably increased in length by the addition of alcohol within the region of concentration covering over from 0.0026 mol/l. to 0.77 mol/l. Addition of alcohol in concentration exceeding 0.77 mol/l. again renders the foam unstable.

(2) Attempts were made to explain the mechanism of foam formation relating to the above phenomena.

(3) Foam and hydrosol were compared with respect to their properties as a disperse system, from which some resemblances as well as differences were pointed out between them.

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(7) The terms, "lyophile Schäume" and "lyophobe Schäume" were also introduced by Bartsch; see the footnote (8).

(8) Bartsch, *Kolloidchem.* Beihefte, **20** (1925), 1.

(9) In the case of emulsion, however, alcohol shows the effect similar to the case of this foam system. In such a case, alcohol is sometimes called "introfier"; see also, Holms, "Laboratory Manual of Colloid Chemistry", 3rd ed., 167, New York (1932).