On the Nature of Foam. VIII. Foam Phenomena of the System Saponin—*i*-Amyl Alcohol—Water.

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(Received May 1, 1943.)

The problems of foam are frequently taken up from the practical stand point, chiefly concerning the determination of the condition of foam formation or destruction. Foam phenomena can also be treated with theoretical interests either because of their being used as a means for observing surface properties of a solution in which they are produced, or of many valuable suggestions obtained by seeking for analogies among foam and other types of dispersion systems, viz., suspension and emulsion.

Now, let us briefly describe the studies on these lines. Ramsden⁽¹⁾ observed that bubbles of a mixed aqueous solution containing two solutes sometimes behave just like those of solutions containing either one of the two components, and this he explained by the selective adsorption at the surface of bubble film. Thus, he concluded in the case of mixed aqueous solutions of two solutes, for example, bile salt–saponin, saponin–egg albumin, and egg albumin–carmin, that the former solutes are adsorbed at the surface of solution with the exclusion of the latter. Similar observations were made by Bartsch.⁽²⁾ Foam of aqueous *i*-amyl alcohol solution is stabilized by the addition of relatively large amounts of glycol or glycerin, but very small amount are sufficient in the case of the addition of saponin, albumin, or gelatin. The former solutes are relatively weakly adsorbed than the latter, and their effects on foam stabilization do not become appreciable unless by the addition of large amounts. The same observation was made upon *i*-amyl alcohol–ethyl alcohol–water system. Bartsch,⁽²⁾ by a number of suggestive experiments, further showed analogies between foam and lyosol as the dispersion systems. According to his idea there are two type of foam, lyophilic and lyophobic, just as in the case of lyosol. The former is produced by shaking a lyophilic colloidal solusion such as an aqueous solution of saponin or soap, while the latter is the foam, for instance, of an aqueous solution of surface active substances such as fatty acids or alcohols. Various resemblances in behaviours between foam and sol were indicated experimentally, mainly concerning the stability of the systems. Ostwald⁽³⁾ measured the life of bubble produced in a mixed aqueous solution of dye and ethyl alcohol, and concluded that the chage in degree of dispersion of the solute affects the life of bubble. Rehbinder⁽⁴⁾ found the relation between the rigidity of foam film and the type of bubble life concentration curve. In the case of less rigid film, the curve shows sharp maximum

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(1) Ramsden, *Z. physik. Chem.*, **47**(1904), 336.
(2) Bartsch, *Kolloid-Z.*, **20**(1925), 1.
(3) Ostwald and Quast, *Kolloid-Z.*, **48**(1929), 156.
(4) Rehbinder and Wenström, *Kolloid-Z.*, **53**(1930), 145.

in life at a certain concentration and decreases to zero at higher or lower concentration of the solute, while, as the bubble film becomes more rigid, the limiting life at concentrated solution grows up from zero to a finite and larger value and the maximum of the curve becomes less marked, and finally disappears.

As for the properties characterizing foam, we can cite its rigidity,⑸ compressibility⑹, liquid or gas contents⑺, and degree of dispersion⑹, of which however detailed studies are not available. One of the present authors also made experiments on foam formation of saponin—ethyl alcohol—water system, and attempted some explanations from the same point of view⑻. To secure more precise informations, foam phenomena of saponin—*i*-amyl alcohol—water system (SAW-system) were studied, and the results were reported in the present paper.

Experiment. We measured the height and life of foam produced in an aqueous solution of SAW-system, where the concentration of saponin was kept constant to 0.0092 g. per litre, while that of *i*-amyl alcohol varied from zero to saturation. Foam is produced by a kind of shaking machine reported in the preceding paper⑻ and in such a manner as discribed in the following; 10 c.c. of the 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 minutes with an amplitude of 12 cm. Height of foam (H), immediately after the stop of shaking, and its life (L), the time required for perfect disintegration of foam, are recorded, from which H—conc. and L—conc. curves are obtained. The results were shown in Table 1, Figs. 1 and 2. We further calculated the reciprocal number of coagulation velocity ($1/V$), namely the stability (S), of foam as a dispersion system.

$$S=\frac{1}{V}=\frac{L}{H}$$

The values were shown in the 5th column of Table 1, and S—conc. curve was depicted in Fig. 3.

The values of L, H, S. for binary mixture of *i*-amyl alcohol and water (AW-system) were measured at the same time for reference, and were also shown in Figs. 1, 2 and 3.

Discussion. (1) First of all, we notice in these figures the pronounced increase in values of S and L at very dilute solution of SAW-system; that is, these begin to increase already at the concentration of $10^{-4.5}\sim10^{-5}$ mol. per liter (called C_0 concentration for convenience) and amount to very large value at the concentration of about $10^{-3.5}$ mol. per litre of *i*-amyl alcohol. These phenomena are striking, as one thousandths or one ten thousandths of *i*-amyl alcohol concentration is sufficient for remarkable foam formation compared with the case of AW-system which, owing to the absence of minute quantities of saponin, posseses a corresponding C_0-value of about $10^{-1.2}$ mol. per litre.

⑸ Derjaguin and Obuchov, *Kolloid-Z.*, **63** (1934), 243.

⑹ Derjaguin, *Kolloid-Z.*, **64** (1933), 1.

⑺ Siehr, *Kolloid-Z.*, **77** (1936), 27.

⑻ Sasaki, this Bulletin, **15** (1940), 449.

Table 1.

Conc. of Saponin (g./l.)	Conc. of *i*-Amyl Alc. (mol./l.)	H (cm.)	L (sec.)	S (L/H)
0	0	0	0	—
0	3.217×10^{-5}	0	0	—
0	1.082×10^{-4}	0.4	1	2.5
0	3.637×10^{-8}	1.3	5	3.84
0	1.223×10^{-3}	1.6	11	1.84
0	1.383×10^{-2}	2.6	19	7.31
0	4.649×10^{-2}	2.7	63	23
0	9.298×10^{-2}	2.8	426	152
0	1.444×10^{-1}	2.4	780	325
0	1.563×10^{-1}	1.9	>900	>473
0	1.701×10^{-1}	1.9	>900	>473
0	1.796×10^{-1}	1.3	>900	>473
0	2.148×10^{-1}	0.7	625	>473
0	2.391×10^{-1}	0	0	—
0	3.202×10^{-1}*	0	0	—
0.0092	0	0.7	ca 62	88.6
0.0092	2.225×10^{-8}	1.0	64	64.0
0.0092	7.483×10^{-8}	0.8	45	56.3
0.0092	2.516×10^{-7}	0.9	41	45.5
0.0092	8.461×10^{-7}	0.7	32	45.7
0.0092	2.845×10^{-6}	0.7	58	82.8
0.0092	9.566×10^{-6}	0.7	68	97.1
0.0092	3.217×10^{-5}	0.9	160	155
0.0092	1.082×10^{-4}	1.6	433	>155
0.0092	3.637×10^{-4}	2.5	>600	>155
0.0092	1.223×10^{-3}	3.1	>600	>155
0.0092	4.112×10^{-3}	3.4	>600	>155
0.0092	1.383×10^{-2}	3.9	>600	>155
0.0092	4.649×10^{-2}	3.5	>600	>155
0.0092	8.941×10^{-2}	3.2	>600	>155
0.0092	1.438×10^{-1}	2.4	>600	>155
0.0092	1.563×10^{-1}	2.4	>600	>155
0.0092	1.622×10^{-1}	2.0	45 min.	>155
0.0092	1.923×10^{-1}	0.8	>600	>155
0.0092	2.090×10^{-1}	0.6	27 min.	>155
0.0092	2.393×10^{-1}	0	0	—
0.0092	3.202×10^{-1}*	0	0	—

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* Indicates saturate solution.

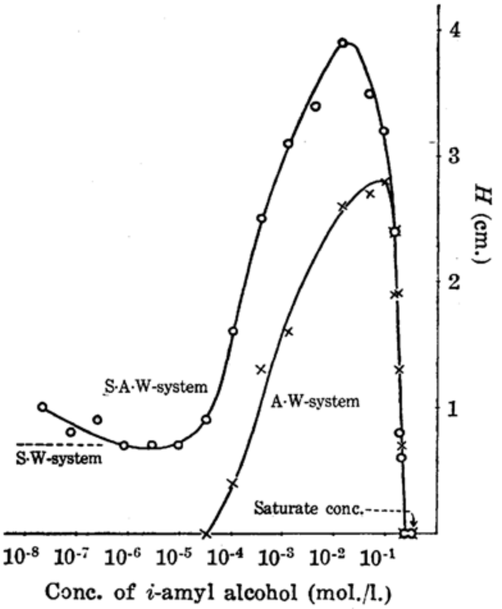

Fig. 1.

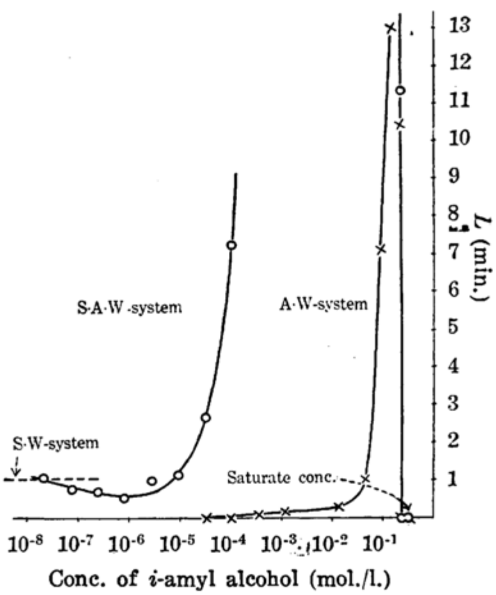

Fig. 2.

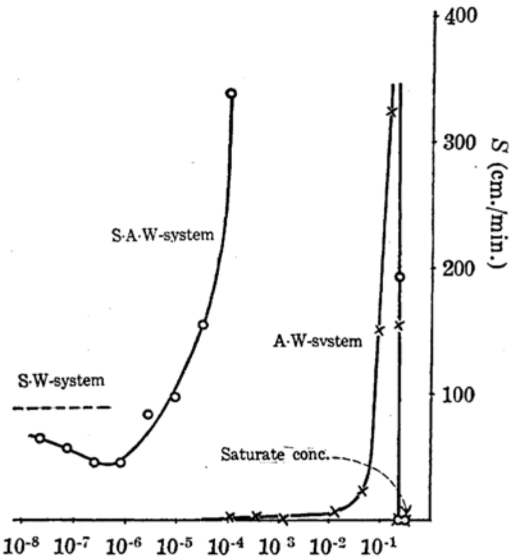

Fig. 3.

When we further compare C_0-value of SAW-system with that of saponin—ethyl alcohol— water system, both of the same saponin concentration (about $10^{-2.8}$ mol. per litre), we recognize that a rule similar to Traube's also holds for C_0-value.

As for the explanation of the increase in amounts of foam formation near the concentration of C_0, we take account of the foam stabilizing action of saponin and the foam producing action of *i*-amyl alcohol, as considered from the relative magnitudes of H to L of SW- and AW-system respectively. In SAW-system near C_0, these two properties affect each other and favour the condition of good foam formation as mentioned in the former report[(8)]. According to this idea, *i*-amyl alcohol here acts as a dispersing agent.

It is interesting to compare the action of alcohols on systems of various types of dispersion. In oil—water emulsions, the addition of alcohol —called sometimes an introfier[(9)]—reduces interfacial tension resulting high dispersion, while in suspensions, namely solid in liquid system, alcohol causes dehydration and coagulation rendering the system unstable. Foam system resembles emulsion rather than suspension from such a point of view. This can be understood when we compare the rigidity or hardness of the interfacial films and the special conditions, coming therefrom, in these three systems of different dispersion types. In the case of suspension the effect of alcohol is mainly confined to its influence upon the stability of the dispersion system already formed, while in the case of emulsion and foam where the interfaces are easily deformable, it frequently happens that we must in addition take account of the effect of alcohol on the degree of dispersion during the formation of the system.

Concerning the stabilizing action, saponin behaves similarly in all three systems of different dispersion types. It is evident in Fig. 3, that in the region of optimum concentration, stability of SAW-system is far larger than expected from the sum of the stability of each component. This is perhaps due to the specific properties of mixed adsorption film described later.

(2) When we examine L—conc. or H—conc. curve of SAW-system for wide range of *i*-amyl alcohol concentration, it may be easily noticed that at the dilute concentration, these curved run closely to those of SW-system, while near the saturation concentration, curves coincide with those of AW-system. In the region of intermediate concentration, the curves neither belong to SW- nor AW-system, and the foam formation is proper to the ternary system itself.

Being regarded as one of the measures of surface properties, the foam phenomena as well as the surface tension tell us the behaviour of liquid surface or frequently more sensitively. It is appearent from Figs. 1, 2, and 3 that the properties of SAW-system below C_0-concentration are characteristic of saponin solute as far as the foam phenomena are concerned. The surface of the solution behaves as if it is a simple solution—here the liquid surface is considered separately as a kind of solution phase —although the bulk phase contains two solutes. Surface activity of *i*-amyl alcohol grows effective at concentrations exceeding C_0 which at least indicates the formation of a mixed adsorption layer consisting of saponin and *i*-amyl alcohol. In the latter case, therefore, both the surface and bulk are mixed solutions. In SAW-system of very high *i*-amyl alcohol

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(9) Holms, "Laboratory Manual of Colloid Chemistry," *3rd Ed.*, 167, New York (1932).

concentration, the foam properties solely coincide with that of AW-system, probably as the result of saturation of adsorption layer with *i*-amyl alcohol, with the exclusion of saponin. In this region, the foam formation of the system decreases to zero shortly before the saturation of *i*-amyl alcohol as it is so with AW-system. *i*-Amyl alcohol often acts as an antifoam under these conditions.

In the above discussion, we attempted to make use of the foam phenomena for the detection of the behaviour of liquid surface, which of course merely suggests one of the possible interpretations of the phenomena observed. These ideas, for instance, were adopted by Ramsden(1) as has been described and also, more recently, by Dunken, Fredenhangen and Wolf(10) who made experiments on the interfacial tension between mercury and *i*-amyl alcohol from the same point of view. The latter authors as well as Ostwald(3) further sought in the bulk of solution for the explanation for changes in surface properties, and pointed out as a factor the alteration in degree of dispersion of the solute. We did not refer so far in the present experiment, but a few properties related to surface and bulk of the solution were measured for further references.

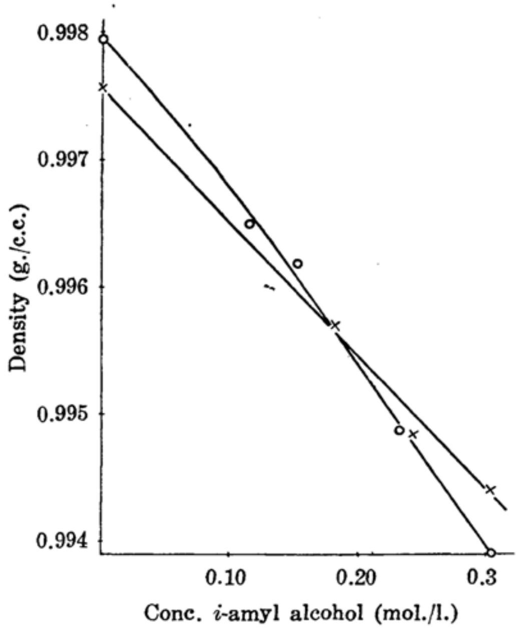

Fig. 4.

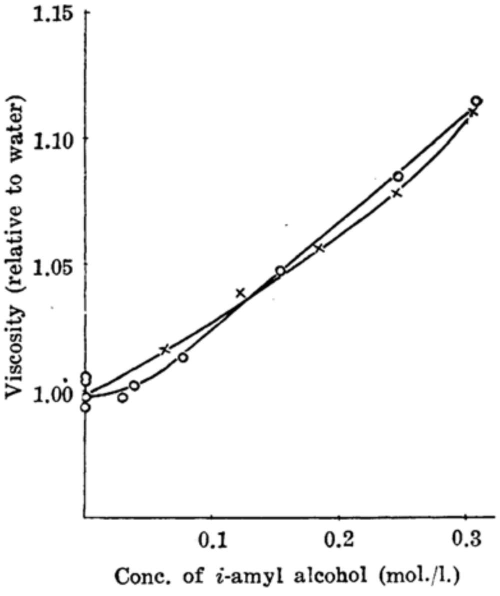

Fig. 5.

Figs. 4 and 5 represent density— and viscosity— *i*-amyl alcohol concentration curves of SAW-system (○) and AW-system (×) respectively. It is indicated in Fig. 5 that there are no differences perceptible in magnitude of viscosity coefficients between aqueous *i*-amyl alcohol solutions with and without saponin. In Fig. 4, on the other hand, we notice that the addition of saponin causes a marked increase in density of dilute

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(10) Dunken, Fredenhangen and Wolf, *Kolloid-Z.*, **95**(1941), 186.

aqueous *i*-amyl alcohol, but the effect becomes less pronounced with increasing concentration and finally saponin decreases the density of the system in the region of sufficiently concentrated *i*-amyl alcohol solution (more than 0.18 mol. per liter). The value of the initial increase in density is far more than the calculated under the assumption of volumes additive for solute and solvent. These increase and subsequent decrease in density may perhaps be explained by a remarkable degree of solvation of saponin and its gradual change. The concentration of 0.18 mol. per litre may also be understood in connection with the strength of solvation. The details, however, are not yet certain.

Further it must be added that both viscosity and density change smoothly with *i*-amyl alcohol concentration, in which we cannot find any explanation sufficient to account for the peculiar nature in foam of SAW-system observed near C_0-point.

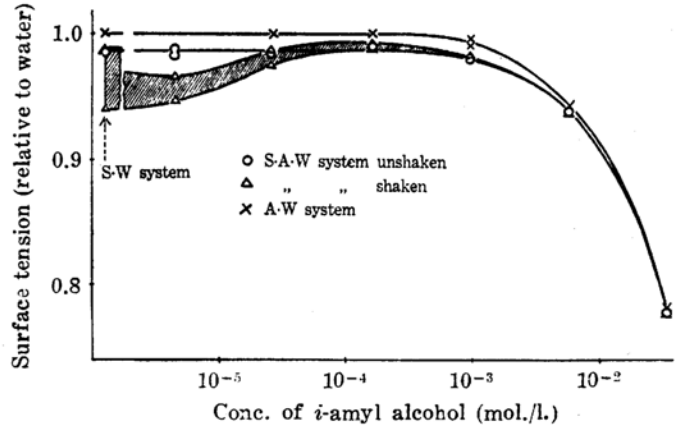

Fig. 6.

Fig. 6 indicates surface tension—*i*-amyl alcohol concentration curves of SAW- and AW- systems (circlet and cross marks respectively). Here we can also neither make distinction between the system with and without saponin, nor find any explanation for the above mentioned peculiarity in foam phenomena. More precise measurement on surface tension, mainly in dilute *i*-amyl alcohol concentration, however, revealed the following interesting but complicated phenomena.

Surface tension of SAW-system often shows change with time. The tension gradually increases with the age of fresh surface and finally reaches to a limiting constant value. The effect is usually more remarkable when we shake a solution shortly before the measurement. These circumstances were also recorded in Fig. 6, in which circlet and cross represent unshaken systems (mentioned above) and triangle, shaken ones. In latter systems, minimum surface tension values of relatively fresh surface and nearly maximum tension often attained after about ten or twenty minutes were recorded for each concentration of *i*-amyl alcohol. Hatching indicates the aging effect. Observed amounts of change in surface tension fluctuate considerably even for one and the same concentration, but as a whole, we can see in the figure that the effect is most remarkable for the system without *i*-amyl alcohol, then it gradually diminishes with increasing concentration and finally disappears at sufficiently high concentration of the alcohol. These phenomena together with the fact that the surface tension of an aqueous *i*-amyl alcohol shows no effect of aging, again as in the case of foam properties, led us to the conclusion that the surface layer of SAW-system changes from simple solution of saponin, through mixed solution of saponin and *i*-amyl alcohol, again to simple solution of *i*-amyl alcohol with increasing concentration of the alcohol. The transition of these surface properties occurs in the region of alcohol concentration of from 10^{-5} to 10^{-2} mol. per litre, which roughly coincides with the case of foam properties.

In connection with surface aging of solutions one question at least is still left unanswered, viz., what is the cause of the phenomena of aging. Such a problem or more generally the questions of surface aging of colloidal solutions have been treated by a number of workers⁽¹¹⁾ and the present authors also have intension to continue their investigations on these lines. Here, we merely point out that such aging phenomena often appear in SAW-system immediately after shaking, while they disapper when we prepare the system without shaking. We need further investigations.

Regarding the foam phenomena as a measure of surface properties, we can trace the behaviour of liquid surface by the observation of the change in magnitude of foam formation as mentioned above. As for the mechanism of foam formation, on the other hand, it is another problem. In SAW-system near C_0 the degree of foam formation as has been was described, enormously increases without any measurable changes or singularities in surface tension, density and viscosity of the system. Thus at least we failed to seek for a simple explanation. These are sufficient to suggest the existence of some other factors or ideas which must be introduced to explain the mechanism of foam formation. In the previous and present reports, we adopted the conception of foam producing power and foam stability,⁽⁸⁾ but they are rather conventional ones which require further explanations based on more fundamental physico-chemical properties well defined.

The expense for the experiments has been defrayed from the grants of Japan Society for the promotion of Scientific Research as well as from that of the Scientific Research Expenditure of the Department of Education to which the authors' thanks are due.

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(11) du Noüy, "Surface equilibria of colloids," New York (1926); Doss, *Kolloid-Z.*, **87** (1939), 272; Boutaric and Berthier, *Bull. Soc. Chim. France*, **6** (1939), 804; Hauser and Swearingen, *J. Phys. Chem.*, **45** (1941), 644; Alexander, *Trans. Faraday Soc.*, **37** (1941), 15; Mc Bain and others, *J. Am. Chem. Soc.*, **62** (1940), 1319; **63** (1941), 1422; Harkins and Nutting, *J. Am. Chem. Soc.*, **62** (1940), 1496; Nutting and Long, *J. Am. Chem. Soc.*, **63** (1941), 84.