Studies on Foams. (I).
The Foaminess and Foam Stability of Liquid Mixtures.

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Introduction. It is often said that the foaminess and the foam stability of liquid are not always parallel with each other. For example, an aqueous solution of saponin produces a more stable but less voluminous foam than that of n-butyl alcohol, when they are shaken under the same condition. It is known, however, that saponin solution readily forms solid skin on their surface, so the structure of foam of the solution may differ entirely from those of alcohol solution. Under these circumstances, it may be more reasonable to compare solutions of common constituents but varying compositions than to compare solutions of different constituents, in order to see whether foaminess and foam stability are parallel or not. By such reason, mixtures of the liquids of low molecular weights were tested, because they make no skins on their surfaces.

The Foam Formation of the Ternary System, Ethyl Alcohol-Glycerol-Water. Foam formation has been tested with a test tube of 18.5 c.c. capacity containing 10 c.c. of solution by shaking up and down with hand for 30 min. at the rate of 3 times per sec. in the amplitude of 25 cm. The following three quantities have been measured: the height of foam zone immediately after the end of shaking, (A_0), which measures foaminess; the time required for a part of liquid surface to appear as a result of collapse of foam zone, (t), that is the duration of foam zone; the time required for whole bubbles to disappear after the appearance of a part of liquid surface, (Δt). The value of Δt is the time expended to disappear by the bubbles arranged in one sheet all over the cross section of the test tube of diameter 1.5 cm., so that this is a measure of the strength of the liquid lamina constituting the upper surface of each bubble.

Relations between the composition of the ternary system expressed by weight per cent and the quantities of A_0, t, and Δt are shown in Fig. 1, 2, and 3, respectively. In these figures, W, E, and G represent water, ethyl alcohol. and glycerol respectively ; PQ are 45 per cent line of ethyl alcohol. In Figs. 1 and 2, two maxima A and B, the latter including B′ which is regarded as the extension of B, are observed, and A_0 and t become nearly zero when the composition of glycerol is increased. On the contrary, in Fig. 3, maximum C is observed in the range of high concentration of glycerol, besides two maxima A and B described above. The new maximum C is extended toward W and covers the maximum B′.

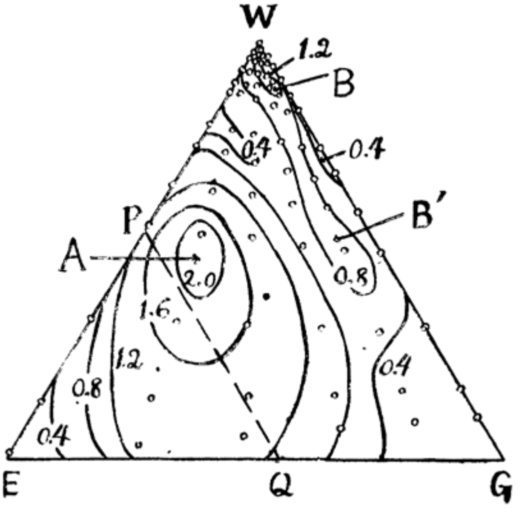

Fig. 1. A_0 (cm.).

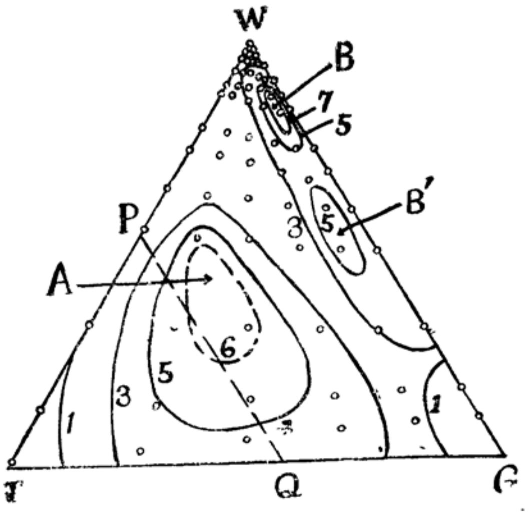

Fig. 2. t (sec.).

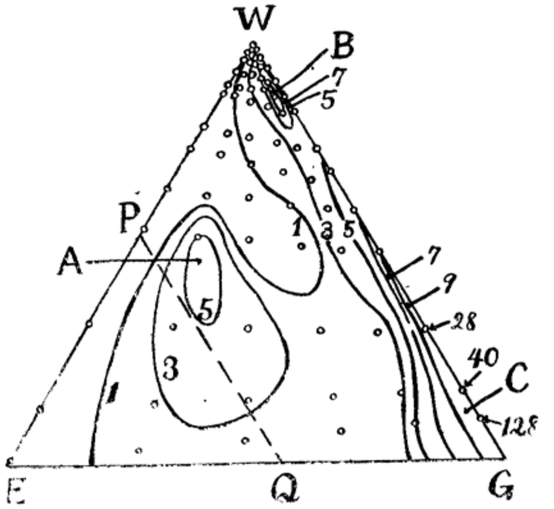

Fig. 3. Δt (sec.).

Foaminess and Foam Stability. Three quantities A_0, t and Δt, are not independent but related one another as follows:—

Bubble stability Δt is thought to be proportional to the duration of a single bubble, which is directly subject to the strength of liquid lamina constructing the upper part of a bubble.

Duration of foam zone t is thought to be subject to both the duration of each bubble (Δt) and the amount of bubbles in the foam, the latter being proportional to the foam zone height (A_0). Among these, A_0 is more predominant to t, since Fig. 2 is entirely parallel to Fig. 1 but not to Fig. 3.

At last, foam zone height A_0 is considered to be the superposition of two actions; the one is to form bubbles by the mixing of gas with liquid, and the other is to make bubbles escape from liquid. If, then, the rate of formation of bubbles by the admixture of gas and liquid is nearly constant under the same conditions of shaking, the foam zone height A_0 should be proportional to bubble stability Δt. Actually, this circumstance is realized near the maximum A and B as is shown in Figs. 1 and 3. As an exception, A_0 and Δt are not parallel in the neighbourhood of G, where the viscosity of the system is larger than ten times of that of water. As easily seen, the duration of bubble once formed, Δt, is largely increased, when the viscosity of liquid is increased, owing to the diminution of the velocity of flow in a liquid lamina. This idea(1) is stated early by J.W. Gibbs, which is referred to recently by S. Ross,(2) G. D. Miles, Leo Shedlovsky and J. Ross.(3) On the one hand,

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(1) S. Berkman and G. Egloff, "Emulsions and Foams," p. 141, New York (1941).

(2) S. Ross, *J. Phys. Chem.*, 47, 266 (1943).

(3) G.D. Miles, Leo Shedlovsky and J. Ross, *J. Phys. Chem.*, 49, 93 (1945).

however, the mixing of gas with liquid is considerably obstructed by the high viscosity, and foam zone height A_0 becomes nearly zero, as supposed by E. G. King.(4)

The Foam Formation of Sulphuric Acid Solutions. Another example that the foaminess and foam stability are not parallel owing to the high viscosity of system is shown in Table 1, with respect to the aqueous solutions of sulphuric acid. Viscosity values taken from the "International Critical Tables" are also cited in the last column. Zero of foaminess or foam duratien means that the shaking does not produce enough bubbles to cover all over the surface, and bubble stability corresponding to them shows the time required for the bubbles to disappear. From this table, the decrease of foaminess and foam duration and the increase of bubble stability are distinctly recognized when the viscosity of system becomes more than eight times as large as that of water.

Table 1. Sulphuric Acid.

Concentration Weight per cent	Foaminess A_0 (cm.)	Foam Duration t (sec.)	Bubble Stability Δt (sec.)	Relative Viscosity (η/η_W)
91.1	0.0	0.0	28	26.3
79.4	0.0	0.0	11.7	22.0
62.3	0.0	0.0	5.3	7.7
41.4	0.4	2.0	0	3.2
21.8	0.4	2.0	0	1.8
0.0	0.4	1.9	0	1.0

Physico-Chemical Properties of the Ternary System. Some physico-chemical properties of the ternary system, ethyl alcohol-glycerol-water are measured, to interpret maxima A, B and C in the diagrams of foam formation of the system. Viscosity, measured by Ostwald's viscometer at 30°C, surface tension by Traube's staragmometer at room temperature 17°C, and density by Ostwald's pycnometer at 30°C, are shown in Figs. 4, 5 and 6, respectively. These are shown, referring to those of water as unity. The volume contraction on admixture calculated from the density data is also shown in Fig. 7 in c. c. per 100 g. of solution.

The Interpretation of Maxima in Foam Formation. The maximum B in Figs. 1, 2 and 3 found in the region of low concentration of ethyl alcohol is thought, as is often said, to be due to the surface activity of ethyl alcohol, referring to Fig. 5, where steep diminution of surface tension of the system is recorded in this region. The maximum C in Fig. 3 is supposed, as already pointed out, to be due to the high viscosity

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(4) E.G. King, *J. Phys. Chem.*, 48, 141 (1944).

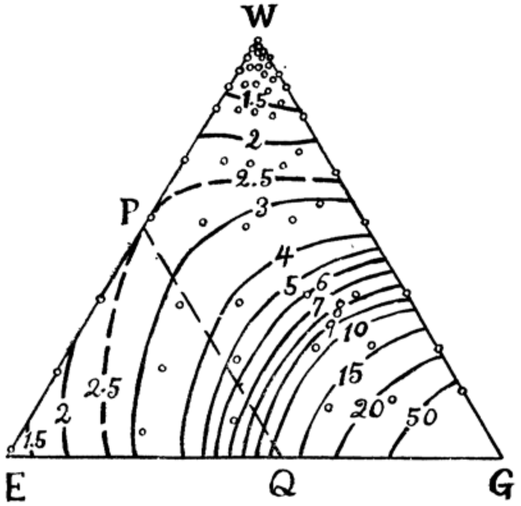

Fig. 4. η/η_w.

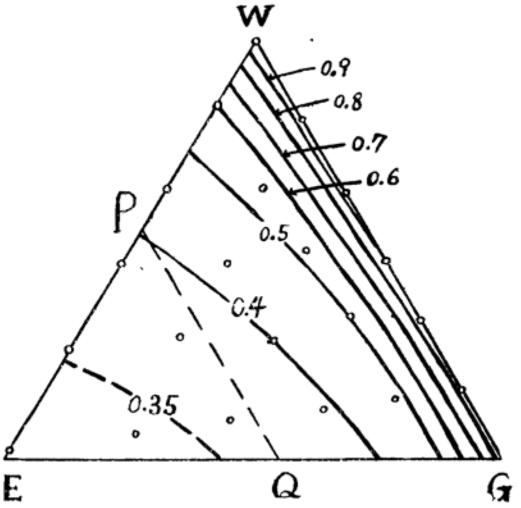

Fig. 5. γ/γ_w.

of the system. Comparing Fig. 3 with Fig. 4, it is noticed that the maximum C is abnormally biassed to the portion of the low concentration of ethyl alcohol, which is not found in the viscosity-composition diagram. This effect is already recognized by O. Bartsch,(5) and the interpretation is that the surface active alcohol drives out the surface inactive glycerol from the wall of foam.

Then how the maximum A in Figs. 1, 2 and 3 is interpreted? Referring to the data cited before, it is found that the density and the surface tension have no relation to this maximum A in foam formation.

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(5) O. Bartsch, *Kolloid-Beihefte.*, 20, 1 (1925).

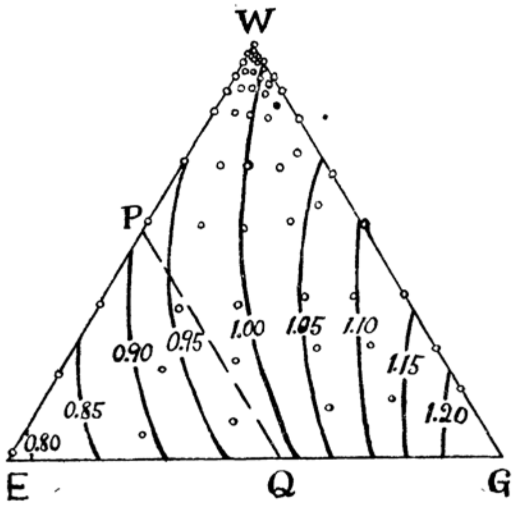

Fig. 6. *d.*

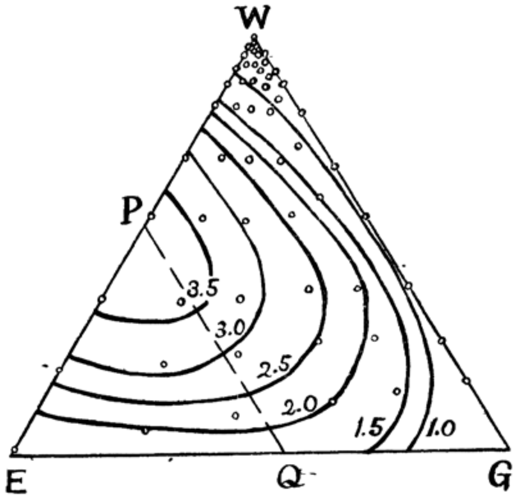

Fig. 7. ΔV (c c./100 g.)

This maximum may be interpreted, by the assumption that the volume contraction on admixture is in close connection with foam formation and viscosity has an auxiliary influence to it; that is to say, the general feature of the maximum A is parallel to the volume contraction ΔV in Fig. 7, and the slope of the maximum A on the side of P is influenced by the viscosity change of the system. Volume contraction might suggest a certain structure formation in the solution that is in favour of foaming. Such an idea, however, should be examined by further examples.

Summary. The height of the foam zone, the duration and the

stability of foam of the ternary system, ethyl alcohol-glycerol-water have been measured. As the result three maximum points A, B and C in the diagrams of these properties are found. The maximum B in the region of low concentration of ethyl alcohol is due to the decrease of surface tension. The maximum C, which is found in the bubble stability diagram while absent in foaminess and foam duration diagrams, may be ascribed to the high viscosity of the system. The same effect is found also in the case of the aqueous solution of sulphuric acid. The maximum A is supposed to be parallel to volume contraction on admixture.

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