On the Nature of Foam. II. The Foam Formation of Ternary System, Acetic Acid—Ethyl Ether—Water.

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It was reported in the preceding paper⁽¹⁾ that the maximum point of the foam stability of the binary mixtures such as water and alcohols or fatty acids occurs at the concentration where the gradient of surface tension is maximum. It was further confirmed that more stable foam can be obtained by the addition of a proper amount of ethyl ether to these solutions. The foaming properties of the ternary solutions is not yet studied quantitatively, though a few qualitative or semi-quantitative experiments have already been published by some authors.(2) (3) (4) (5) (6) The present paper describes the investigation on the foam formation of ternary liquid system, acetic acid—ethyl ether—water (AEW-system).

Experimental Procedure. In the ternary system of AEW, acetic acid is soluble both in ether and in water while ether is hardly soluble in water. Mutual solubility curve of this system is obtained by the measurement of the volume ratio in the liquid which shows the first indication of turbidity by the addition of the insoluble component to the homogeneous mixture of the other two. Fig. 1 is the diagram of AEW-system thus obtained, the data of which being shown in Table 1. Measurements were carried out at about 20°C.

The tie-line, i.e. the straight line connecting the two points on the mutual solubility curve which represents coexisting phases of a heterogeneous system can be obtained as follows: We take any one point in the heterogeneous region of the diagram, and draw a straight line so as its section made by the mutual solubility curve is divided at that point in two portions, the ratio of which is equal to that of the volumes of upper and lower coexisting phases. The tie-lines thus obtained are shown in Fig. 1.

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

(2) Wo. Ostwald and A. Steiner, *Kolloid-Z.*, **36** (1925), 342.

(3) C. W. Foulk, *J. Ind. Eng. Chem.*, **16** (1924), 1121; **21** (1929), 815.

(4) R. H. Bogue, *J. Am. Chem. Soc.*, **44** (1922), 1343.

(5) Wo. Ostwald and A. Quast, *Kolloid-Z.*, **48** (1929), 156.

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

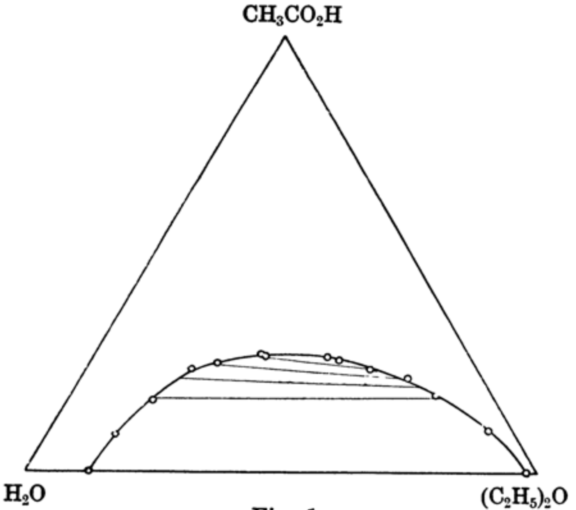

Fig. 1.

Table 1.

Volume ratio of limiting turbid mixture (about 20°C.).

Acetic acid	Ethyl ether	Water
0	12.3	87.7
0	98.0	2.0
8.7	13.5	77.8
9.5	85.7	4.8
16.7	16.7	66.6
17.8	71.5	10.7
21.6	64.0	14.4
23.8	20.6	55.6
23.8	55.6	20.6
25.0	25.0	50.0
25.8	48.4	25.8
26.4	46.0	27.6
26.5	33.8	39.7
27.0	32.5	40.5
60.0	40.0	∞
70.0	∞	30.0

Measurements of the foam formation were then undertaken for homogeneous and heterogeneous systems of AEW. The apparatus employed in the present experiment is different from that described in the preceding paper.⑴ It has been constructed as shown in Fig. 2. In this figure, M is a synchronous motor, W a wheel carrying a crank, S a brake acting upon W, P a handle connected to the axis Q of the wheel W by a cord, R a spring pulling Q to S, and A a glass stoppered test tube with its support.

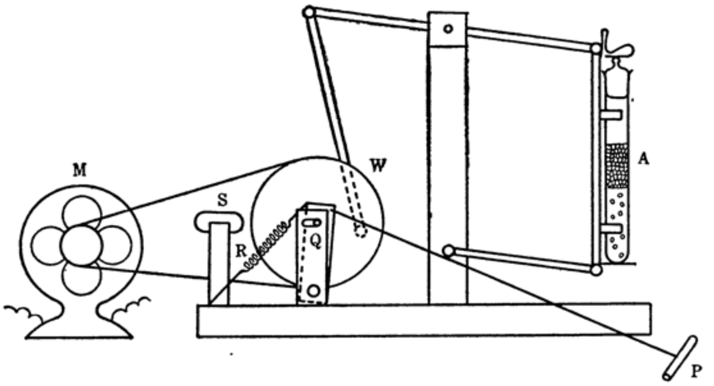

Fig. 2.

By pulling handle P, wheel W starts to rotate and test tube A vibrates up and down. If we release P, wheel W is pulled back by spring R, and brake S acts to stop the wheel instantaneously. By this arrangement, the vibration can be made to start or stop sharply. Amplitude of the vibration is 12 cm. and the frequency is kept constant to 300 vibrations per minute throughout this experiment.

Measurement of the foam formation has been carried out as follows: First, a well stoppered test tube of 1.5 cm. in diameter and 15 cm. in length is washed carefully with soap solution and with chromic acid mixture successively, steamed with water vapour, and dried in an air bath. Then 10 c.c. of the liquid for measurement is introduced into the tube (up to the height of about 6 cm. from bottom) which is stoppered immediately and fixed on the shaking apparatus. Then the motor is set in motion and the test tube is brought into vibration by pulling the handle P. After continuing vibration for 10 seconds, it is stopped by releasing the handle and the two following quantities are measured: (1) Height of foam zone (*H*) which is measured immediately after the stop of vibration by reading the upper and lower meniscuses of foam zone by the scale attached to the test tube. (2) Time of duration of the foam zone (*S*) which is measured by recording the time required from the moment of stop of motion to the complete collapse of foam zone.

Table 2.

Composition in volume ratio			Height of foam, H(cm.)	Stability of foam, S(second)	Degree of foam formation, $S \cdot H$
Acetic acid	Ethyl ether	Water			
0	1.25	8.75	0	0	0
0	9.80	0.20	0	0	0
0.50	0	9.50	1.4	6.4	9.0
0.50	1.00	8.50	2.8	12.7	35.6
0.60	5.50	3.90	0	0	0
0.70	0	9.30	3.0	8.8	26.4
0.80	7.20	2.00	1.1	1.0	1.0
1.00	0.50	8.50	2.3	10.6	24.4
1.20	1.40	7.40	0	0	0
1.20	4.80	4.00	0	0	0
1.50	0	8.50	2.5	11.2	28.0
1.50	1.00	7.50	1.8	10.7	19.3
1.70	4.00	4.30	0	0	0
1.80	1.70	7.50	0	0	0
1.85	7.35	0.80	1.2	1.3	1.6
2.00	8.00	0	0	0	0
2.10	1.40	6.50	1.9	9.1	17.3
2.10	3.70	4.20	0	0	0
2.10	4.90	3.00	1.3	1.4	1.8
2.35	4.15	3.50	1.2	1.9	2.3
2.40	3.80	3.80	0	0	0
2.40	5.60	2.00	2.1	3.3	6.9
2.50	0	7.50	1.3	4.9	6.4
2.50	2.50	5.00	0	0	0

Table 2.—(*Concluded*)

Composition in volume ratio			Height of foam, H(cm.)	Stability of foam, S(second)	Degree of foam formation, $S\cdot H$
Acetic acid	Ethyl ether	Water			
2.62	3.88	3.50	0	0	0
2.63	2.63	4.74	2.0	34.7	69.4
2.65	4.60	2.75	2.6	7.0	18.2
2.70	4.00	3.30	2.6	51.9	134.9
2.75	2.75	4.50	2.3	22.7	52.2
2.80	4.20	3.00	2.7	15.1	40.8
3.00	2.00	5.00	3.1	6.3	19.5
3.00	3.00	4.00	2.5	13.3	33.3
3.00	4.50	2 50	2.8	4.5	12.6
3.15	0.35	6.50	1.8	3.6	6.5
3.40	3.60	3.00	2.2	4.4	9.7
3.40	5.10	1.50	1.1	1.3	1.4
3.50	0	6.50	0.9	1.9	1.7
4.00	1.00	5.00	3.1	2.4	7.4
4.00	6.00	0	0	0	0
4.20	2.80	3.00	1.7	2.6	4.4
5.00	0	5.00	1.8	1.7	3.1
5.60	1.40	3.00	1.8	1.9	3.4
6.00	4.00	0	0	0	0
7.00	0	3.00	1.1	1.6	1.8
8.00	2.00	0	0	0	0

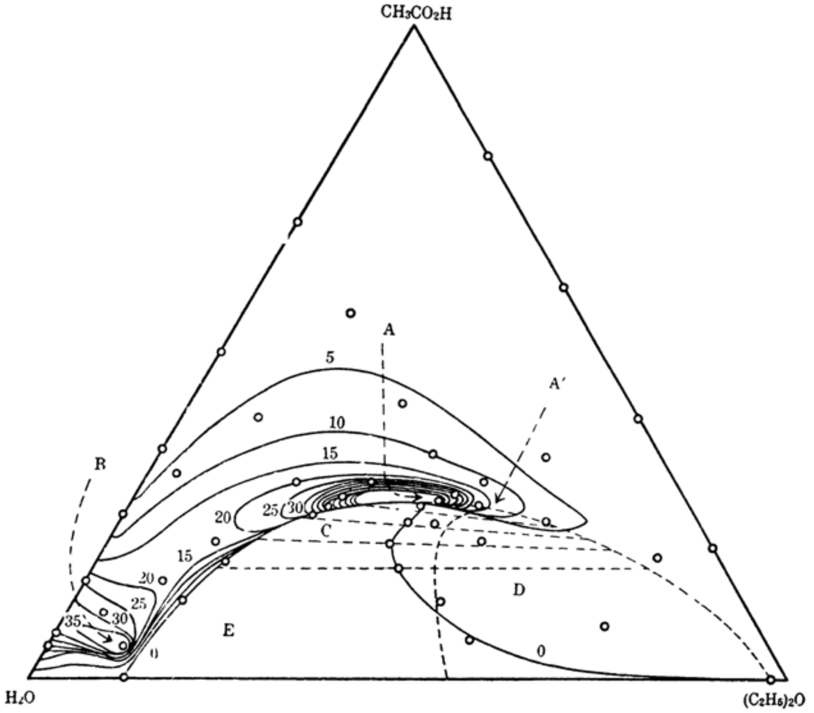

Fig. 3.

Experimental Results. The results of measurements are shown in Table 2.(7) In this table, S and H denote the time of duration and the height of foam zone respectively. As the measure of foam formation, S,(5)(6)(8) H,(2)(4)(9) or S/H(10) may be adopted. In this paper, however, both S and H were considered to be separate and independent factors characterizing the foam formation, and the product of them was employed as denoting the degree of foam formation. Fig. 3 is the diagram obtained from the above data and it represents the relation between composition and foam formation of AEW-system.

Discussion. The diagram of the foam formation, as a whole, is separated into two regions by the mutual solubility curve, namely homogeneous and heterogeneous regions.

(1) *Homogeneous region.* All systems of this region can froth, though widely differing in its degree, and the strong foam formations are observed in the vicinity of two points A and B in Fig. 3. Further, the surface of diagram has the steepest slope along the mutual solubility curve and along the straight line connecting the vertices of water and acetic acid, while it has gentle slope towards the straight line connecting water and ethyl ether.

The fact that the system near point B foams remarkably is explained from the results of the former experiments,(1) i.e. water—acetic acid system has the maximum foam stability at the region of such a dilute solution as its surface tension rapidly falls with dilution, and near this region point B exists. This can readily be seen in Fig. 3.

Foam formation also shows its maximum at point A and its degree far more exceeds that at B. The surface of diagram is remarkably projected near point A. For the explanation of the foam formation of systems near that point, it is necessary to study some other systems showing the same singularity upon the foam formation, or any other phenomena relating to it. As for an instance of the phenomenon exhibiting a similar singularity to foam formation, there is the critical opalescence of ternary systems consisting of benzene, ethyl alcohol and water or the analogous systems which were studied by Sata and his co-workers.(11) It is briefly explained as follows:

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(7) Only a part of the data was shown for the economy of spaces.

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

(9) Wo. Ostwald and M. Meisser, *Kolloid-Beihefte*, **26** (1928), 1.

(10) P. A. Rehbinder and A. A. Trapeznikov, *Compt. rend. acad. sci. U. R. S. S.*, **18** (1938), 423.

(11) N. Sata and O. Kimura, this Bulletin, **10** (1935), 409; O. Kimura, *ibid.*, **11** (1936), 57; N. Sata and Y. Niwase, *ibid.*, **12** (1937), 86.

When we continue to add water to a homogeneous mixture of benzene and ethyl alcohol, the whole system gradually approaches to a region of heterogeneous system, becomes heterogeneous at last, and separates into two layers. Some systems show critical opalescence and anomalous increase in viscosity just before the separation into two layers, while others do not. There are optimum composition for initial benzene—ethyl alcohol mixture to show such critical opalescence on addition of water and the region of compositions of these opalescent systems is given by these authors as shown in Fig. 4. This is also a narrow region along a portion of the mutual solubility curve, and roughly corresponds to region A in Fig. 3. Taking into account of the above phenomena, a tentative explanation of the foam formation of systems near point A is made as follows:

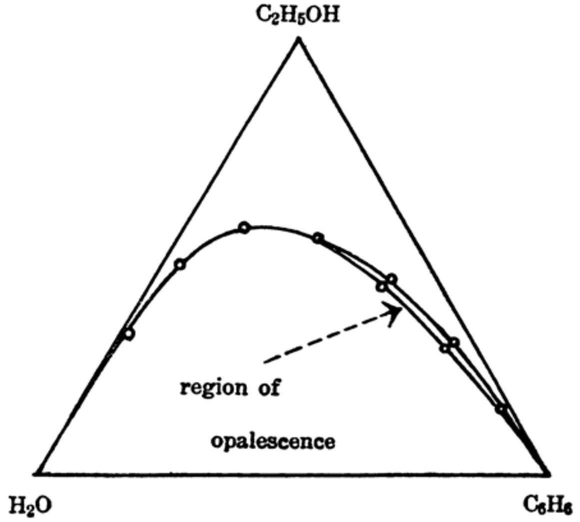


Fig. 4.

When we trace the locus of middle points of tie-lines in the diagram of Fig. 3, we can find that region A is situated not far off the point of intersection of this locus and mutual solubility curve (A′ in the diagram). By the addition of small quantity of insoluble component (in this case water), any homogeneous system belonging to such a region can readily be converted into a heterogeneous one consisting of upper and lower layers of almost equal volumes, equal densities, and very small interfacial tension between them. Such conditions are generally considered to favour the formation of emulsion and consequently the foam is mechanically stabilized in such system like in most other colloidal solution.(2) Critical opalescence and anomalous viscosity which can only be seen in this region also be explained as the typical phenomena of emulsion. Further, the aqueous solution of butyric acid was reported to show a similar critical foam formation.⁽²⁾

It has often been said that the foam of a solution vanishes at the moment when it touches ethyl ether or even the vapour of ethyl ether. This case, however, differs from the present condition, and belongs to the heterogeneous region or the formation of heterogeneous film by the condensation of ether vapour on the bubble wall, which is discussed in the later section. The mixture of the composition corresponding to region A in Fig. 3 has an outstanding power of foaming.

(2) *Heterogeneous region.* It can readily be seen from the diagram of Fig. 3, that the heterogeneous region is further divided into two parts, i.e. foamy and non-foamy regions.

(a) First, we will consider region C in Fig. 3 which is adjacent to region A. In a heterogeneous system belonging to this region, an upper layer consisting of water, acetic acid, and excessive ethyl ether is considerably smaller in volume compared with a lower layer consisting of acetic acid, ethyl ether, and excessive water, while the surface tension of the former is smaller than that of the latter, but not so markedly as in the system of region E. Table 3 shows these relations.

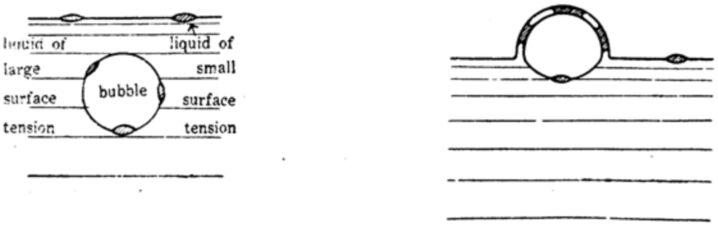
Table 3.

Composition in volume ratio			Surface tension (relative)		Foam formation	
Acetic acid	Ethyl ether	Water	Upper layer	Lower layer	$V_u < V_l$*	$V_u > V_l$
2.50	4.40	3.10	0.309	0.341	↑C region in Fig. 3, non-foamy.	D region in Fig. 3, slightly foamy.
2.20	4.30	3.50	0.301	0.368		
1.70	4.50	3.80	0.292	0.402	E region in Fig. 3, emulsion drop contains bubble.↓	
1.00	5.00	4.00	0.278	0.464		
0	5.50	4.50	0.261	0.632		

* V_u and V_l denote volumes of upper and lower liquids respectively, coexisting in the corresponding heterogeneous system.

When we shake a system under such conditions, the upper layer of relatively small volume is dispersed in the lower one, and droplets of emulsion thus produced are then brought to the surface of bubbles formed at the same time by shaking, or they flock together in the free surface of dispersing medium. They finally spread upon the surface of the film enveloping the foam and flattly occupy a portion of it as is illustrated in

Fig. 5. Thus the patches of small surface tension make the film unstable and the bubbles will burst itself.(12) Heterogeneous systems consisting of fatty acids, alcohols, or any other water insoluble surface active substance and its aqueous solution as studied in the preceding experiments(1) also break the foam by the same reason.



Hatching indicates an upper layer of liquid of the heterogeneous system.

Fig. 5.

Fig. 6.

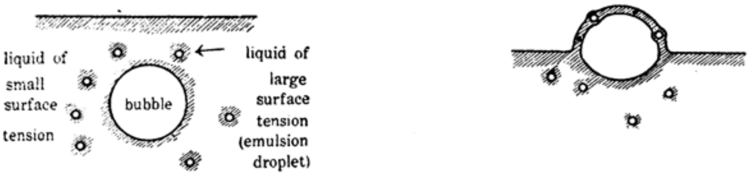


Fig. 7.

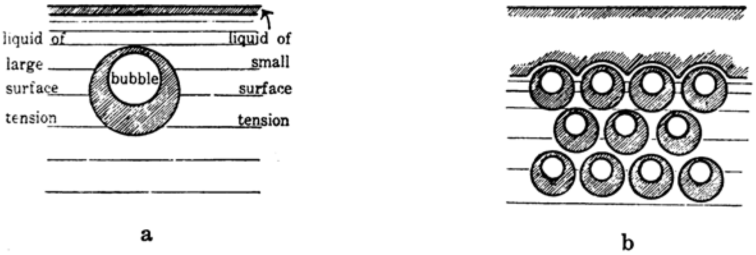


Fig. 8.

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

(b) On the other hand, there can be a case where the foam is somewhat stabilized in a heterogeneous system in which a lower layer becomes to be dispersed in an upper one, or an upper layer of markedly lower surface tension is dispersed in a lower one on agitation. We may discuss the former case in this section.

Such a heterogeneous system usually consists of an upper layer of larger volume and a lower layer of smaller one as shown in the last column of Table 3, which corresponds to region D in Fig. 3. When we shake AEW-system belonging to this region, the lower layer of at least slightly larger surface tension is dispersed in the upper one which can readily be recognised from the appearance of breaking up of emulsion thus formed.(13) Droplets of such emulsion do not break films of foam produced in it simultaneously by agitation, for they either form droplets (and do not spread) on the surface of film in the case when they have slightly larger surface tension than dispersing medium, or they utterly escape from the surface of film when they have fairly larger surface tension than dispersing medium. These are schematically illustrated in Figs. 6 and 7 respectively. Accordingly, the system does not interfere with the foam produced in the dispersing medium, and so certain degree of foam formation can be expected in these cases.

(c) Next, the latter case of the section (b) will be discussed, that is the heterogeneous system composed of the droplets of markedly smaller surface tension in the medium of larger surface tension. In such a system, the volume of the upper layer (smaller surface tension) is usually smaller than that of lower one (larger surface tension) as shown in lower portion of the sixth column of Table 3, which corresponds to region E in Fig. 3.

When we shake AEW-system of this region, air bubbles produced at the same time in the dispersing medium readily and entirely go into the interior of emulsion droplets on account of large difference in surface tensions between both layers, so bubbles are covered with homogeneous films made of emulsion droplets which are again surrounded by the dispersing medium. These circumstances are readily understood from Fig. 8a. Thus, in the suitable system of this region, we can observe fairly stable emulsion drops containing air bubbles which gradually go up to, and accumulate at, the interface of ethyl ether—water as shown in Fig. 8b, though the foam formation cannot be observed.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima for his kind guidance. The expense for the experi-

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(13) It will be reported precisely upon this point in the latter paper.

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Summary.

(1) The foam formation of the liquid ternary system of acetic acid—ethyl ether—water was measured by means of a shaking apparatus which was properly constructed for this purpose.

(2) The life time of foam produced and the height of foam zone have been measured.

(3) The diagrams were made between the degree of foam formation and the composition, and several conclusions were obtained on the foam formation of the mixture belonging to homogeneous and heterogeneous regions of the above ternary system.

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