On the Nature of Foam. III. The Foam Formation of Ternary System, Acetic Acid—Benzene—Water.

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The foam formation of the ternary system of acetic acid–ethyl ether–water (AEW) was reported and some explanations were given in the preceding paper.[1] It was further confirmed that the ternary system of acetic acid–benzene–water (ABW) shows a similar behaviour in the foam formation to the system of AEW. The present paper describes the investigation of the foam formation of the ternary liquid system of ABW.

Experimental Procedure. In the ternary system or ABW, benzene is insoluble in water, while acetic acid is soluble in all proportions both in water and in benezene. The mutual solubility curve and tie-lines of this system are obtained by the same methods as were described in the preceding paper,[1] and the data of which are given in Tables 1 and 2, respectively. These data are depicted in Fig. 1. To draw tie-lines, we take one point corresponding to the composition given in Table 2, which is situated in the heterogeneous region of Fig. 1, 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 being equal to that of corresponding volumes of upper and lower layers shown in Table 2.

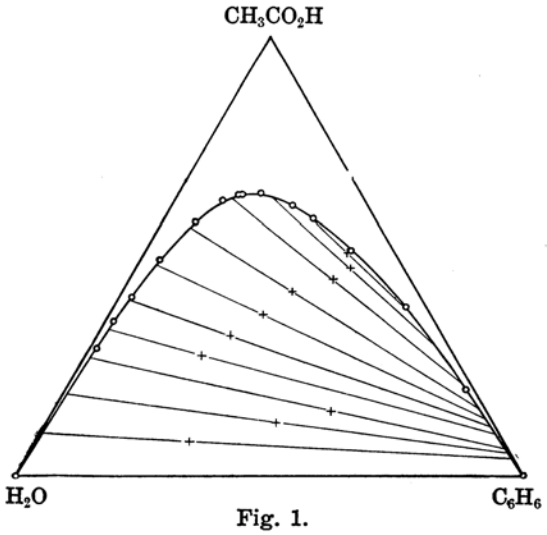

Fig. 1.

Measurements of the foam formation were then undertaken by means of the shaking apparatus in the same manner as was described in the preceding paper.[1] Thus the foam height H and the stability S have been measured after ten seconds' shaking of a solution with the frequency of 300 vibrations per minute at about 20°C.

Experimental Results. The results of measurements are shown in Table 3.[2] Here, the product of S and H is considered to be the measure of the foam formation. Fig. 2 shows the diagram which represents the relation between composition and foam formation of ABW-system.

(1) Sasaki, this Bulletin, **13** (1938), 669.
(2) Only a part of the data are shown for the economy of spaces.

Table 1.

Volume ratio of limiting turbid mixture (about 20°)		
Acetic acid	Benzene	Water
0	0	10.00
1.98	7.90	0.12
2.92	0.14	6.94
3.53	0.17	6.30
3.85	5.77	0.38
4.10	0.23	5.67
4.93	0.38	4.69
5.15	4.04	0.81
5.80	0.65	3.55
5.89	2.93	1.18
6.17	2.39	1.44
6.28	0.93	2.77
6.40	1.20	2.40
6.41	2.05	1.64
6.42	1.63	1.95
0	10.00	0

Table 2.

Composition in volume ratio			Volume ratio	
Acetic acid	Benzene	Water	upper layer	lower layer
5.10	4.00	0.90	0.625	1.000
4.74	4.21	1.05	0.920	1.000
4.50	4.00	1.50	0.785	1.000
4.21	3.44	2.35	0.578	1.000
3.71	3.05	3.24	0.486	1.000
3.21	2.62	4.17	0.385	1.000
2.80	2.30	4.90	0.322	1.000
1.50	5.50	3.00	1.381	1.000
1.23	4.53	4.24	0.907	1.000
0.82	3.02	6.16	0.452	1.000

Table 3.

Composition in volume ratio			Height of foam, H(cm.)	Stability of foam, S(second)	Degree of foam formation, $S \cdot H$
Acetic acid	Benzene	Water			
0	1.50	8.50	0	0	0
0	2.63	7.37	0	0	0
0.04	4.98	4.98	0	0	0
0.33	5.92	3.75	0	0	0
0.50	0	9.50	2.2	12.5	27.5
0.50	0.80	8.70	3.1	7.0	21.7
0.50	2.00	7.50	2.6	5.9	15.3
0.50	5.00	4.50	1.1	5.1	5.6
0.80	0	9.20	2.2	13.5	29.7
0.80	3.40	5.80	1.4	4.6	64.4
1.00	0	9.00	2.3	15.0	34.5
1.00	1.30	7.70	1.6	7.1	11.4
1.00	2.50	6.50	1.4	4.9	6.9
1.00	4.50	4.50	0.7	2.6	1.8
1.10	4.90	4.00	0	0	0
1.20	0	8.80	2.2	12.6	27.7
1.48	0.10	8.42	1.7	5.8	9.9
1.50	0	8.50	2.5	12.6	31.5
1.50	3.20	5.30	0.6	1.8	1.1
1.60	0.70	7.70	1.4	4.8	6.7
1.95	3.42	4.63	0	0	0
1.98	7.90	0.11	0	0	0
2.00	0	8.00	1.9	9.7	18.4
2.00	1.30	6.70	0.8	3.1	2.5
2.50	1.25	6.25	0	0	0
3.00	0.47	6.53	0	0	0
3.49	1.78	4.73	0	0	0
3.50	0	6.50	1.9	3.0	5.7
3.80	5.90	0.30	0	0	0
4.50	5.00	0.50	1.2	1.5	1.8
4.82	0.38	4.80	0	0	0
4.90	2.50	2.60	0	0	0
4.90	4.32	0.78	1.9	8.4	16.0

Table 3.—(*Concluded*)

Composition in volume ratio			Height of foam, H(cm.)	Stability of foam, S(second)	Degree of foam formation, $S \cdot H$
Acetic acid	Benzene	Water			
5.00	4.40	0.60	1.1	1.4	1.5
5.17	3.90	0.95	0	0	0
5.22	3.94	0.84	1.6	4.9	7.8
5.30	4.00	0.70	1.2	1.8	2.2
5.32	4.68	0	0	0	0
5.90	3.00	1.10	2.0	6.9	13.8
6.00	3.00	1.00	1.6	2.3	3.7
6.15	0.87	2.98	0	0	0
6.32	1.96	1.72	0	0	0
6.48	1.33	2.19	1.6	1.9	3.0
6.50	2.00	1.50	0.8	2.1	1.7
7.00	0	3.00	1.0	1.3	1.3
7.00	1.50	1.50	1.0	1.3	1.3

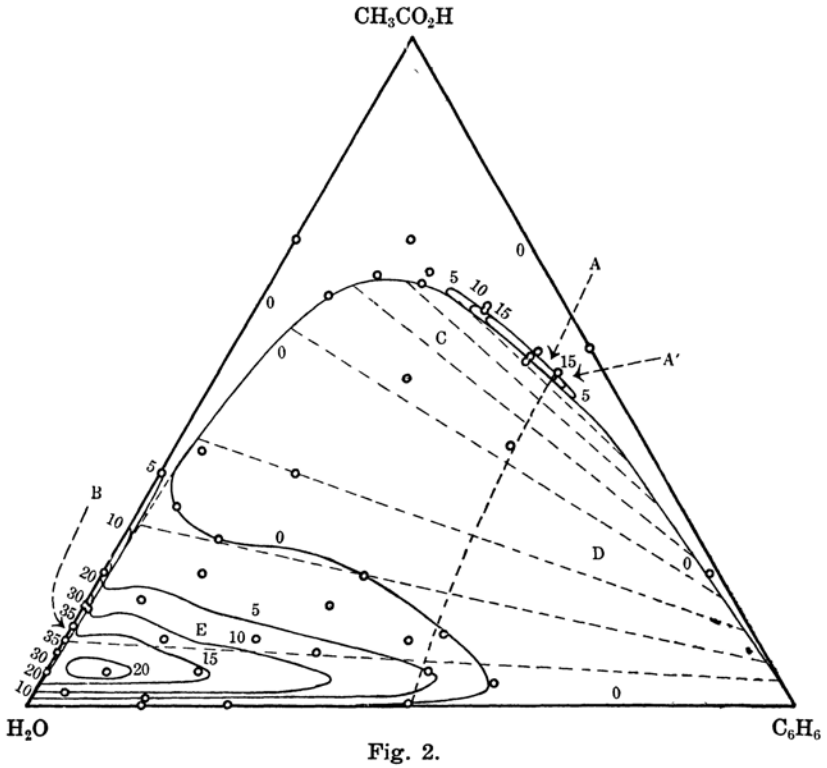

Fig. 2.

Discussion. The diagram of the foam formation of ABW-system, like that of AEW-system, is separated into two regions by the mutual solubility curve, that is homogeneous and heterogeneous regions.

(1) *Homogeneous region.* The surface of the diagram has two maxima of foam formation along the mutual solubility curve at the vicinity of the points A and B in Fig. 2, respectively. The other portions of the

homogeneous region can froth more or less. In this region, the shape of surface of the diagram, as a whole, is analogous to that of AEW-system, and the maximum near the point B is explained from its position being close to the composition of maximum foam formation in the binary system of acetic acid–water, as in the case of AEW-system. In the case of ABW-system, however, homogeneous region near the point B is so narrow that the diagram of this part is composed of two steep surfaces forming a sharp edge as shown in Fig. 2.

The foam formation also shows its maximum near the point A in Fig. 2, but it is less exaggerated in this system than in AEW-system and the height of maximum near the point A is even smaller than that near the point B in ABW-system. The explanation was made in the preceding paper[1] upon the foam formation of the system near the point A, referring to the analogous phenomena of opalescence and anomalous viscosity exhibited by the ternary system of benzene–ethyl alcohol–water, as due to its liability to form emulsion.

In the present case, the conditions are more favourable for this explanation, because the opalescent zone of benzene–ethyl alcohol–water system and the region A in Fig. 2 coincide each other and they are both situated in the vicinity of the point of intersection made by the mutual solubility curve and the locus of middle points of tie-lines (A′ in Fig. 2.). We can explain, therefore, the maximum of foam formation, the critical opalescence and the anormalous viscosity from the colloidal behaviour of corresponding systems.

(2) *Heterogeneous region.* Heterogeneous region may be divided into three parts, namely, region C, D and E in Fig. 2.

(a) Region C. In the system of this region, an upper layer consisting of water, acetic acid and excessive benzene is smaller in volume compared with a lower one consisting of acetic acid, benzene 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 E region. These relations are shown in the sixth column of Table 4.

Table 4.

Composition in volume ratio			Surface tension (relative)		Foam formation	
Acetic acid	Benzene	Water	upper layer	lower layer	$V^* < V_l$	$V_u > V_l$
4.83	3.92	1.25	0.402	0.421	C region in Fig 2, non foamy.	D region in Fig. 2, non foamy.
4.31	3.54	2.15	0.416	0.465		
2.42	4.35	3.23	0.421	0.553		
1.26	5.04	3.70	0.416	0.651	E region in Fig. 2, remarkably foamy. (three layered film)	
0.74	2.72	6.53	0.407	0.740		
0	5.00	5.00	0.419	0.999		

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

When we shake a system of this region, the film of air bubble produced in the liquid becomes heterogeneous and the foam cannot be produced[3] as in the corresponding case of AEW-system.

(b) Region D. This corresponds to the heterogeneous region, the lower layer of which, consisting of acetic acid, benzene and excessive water and having a smaller volume, is dispersed in an upper one consisting of acetic acid, water and excessive benzene. The last column of Table 4 corresponds to this region.

In such system, certain degree of foam formation can be expected on shaking, because emulsion droplets of larger surface tension than the dispersing medium do not interfere with the foam produced in this system as was observed in AEW-system. But in the mixture corresponding to this region of ABW-system, practically no foam can be produced on shaking. It is perhaps because the upper layer of this system does not foam while that of AEW-system foams a little.

(c) Region E. In the heterogeneous system belonging to this region, the upper layer consisting of acetic acid, water and excessive benzene is smaller in volume and markedly smaller in surface tension than the lower one consisting of acetic acid, benzene and excessive water, as shown in the sixth column of Table 4.

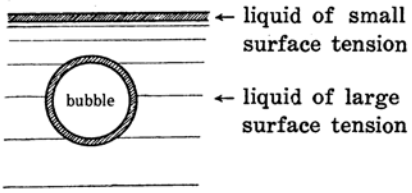

Fig. 3a.

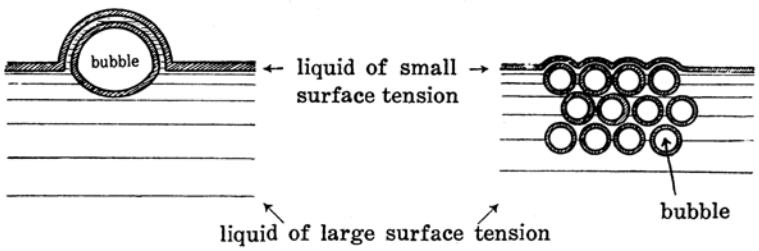

Fig. 3b.

In ABW-system of this region, the upper layer is dispersed in the lower one on shaking. At the same time, air bubbles are also produced both in emulsion droplets and in the dispersing medium, but bubbles in the dispersing medium readily and entirely go into the interior of the emulsion droplets on account of the large difference in surface tension between both layers. Thus, air 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. 3a, as in the case of the corresponding system of AEW.[1]

Such air bubbles go up to and accumulate at the interface of benzene–water, and produce the foam as shown in Fig. 3b. Now, the foam is

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

covered at least by three layers of homogeneous films, of which middle layer is an aqueous mixture of larger surface tension than the outer ones. Therefore, air in bubbles cannot escape towards outside on account of the difficulty in breaking the innermost films (i.e. exposing itself to the middle layer). In other words, the foam is stabilised in such systems.

Although mere emulsion drops containing air bubbles were observed in AEW-system of this region, fairly stable foam is produced in the case of ABW-system. In Fig. 2, relatively larger zone of remarkable foam formation can be seen in the region E. It will be emphasized that these foams, consisting of triple layered films, are entirely different in its nature from the ordinary foams covered with single homogeneous film.

In region E of ABW-system, surface constituting the diagram is steep along the straight line connecting the vertices of benzene and water. This means that a heterogeneous mixture of water and benzene foams considerably by the addition of small quantity of acetic acid. Such phenomenon can also be observed when we substitute benzene for liquid aliphatic hydrocarbon such as hexane. This suggests an interesting practical application of detecting trace of surface active substances usually existing as impurities in hexane or its homologues. Namely, when we shake water with a relatively small volume of hexane which was obtained by the usual method of repeated distillation from commercial products, foam formation may be observed. No foam can be produced, however, in the mixture of water and hexane from which traces of impurities are carefully removed by shaking it for a long time with fuming sulphuric acid and distilling.[4] This is explained from the fact that the impurities mainly consist of surface active substances and behave just like acetic acid in the case of ABW-system.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima for his kind guidance. The expense for the experiments has been defrayed by a grant given to Prof. Sameshima from Nippon Gakujutsu Shinkokwai (Japan Society for the Promotion of Scientific Research), to which the author's thanks are due.

Summary.

(1) The foam formation of liquid ternary system of acetic acid–benzene–water (ABW) has been measured by means of a shaking apparatus, and a diagram has been drawn between the degree of foam formation and the composition.

(2) The foam formation of homogeneous system of ABW is analogous to that of acetic acid–ethyl ether–water (AEW), showing two maxima of foam formation. In the heterogeneous system of ABW, however, remarkable foam-formation can be observed, instead of mere emulsion droplets containing bubbles in the case of AEW-system.

(3) The explanation of foam formation in heterogeneous ABW-system has been attempted.

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(4) A. Weissberger and E. Proskauer, "Organic Solvents," 99, (1935).