On the Nature of Foam. V. Phase Inversion and Foam Formation of Emulsion Consisting of Acetic Acid, Benzene, and Water.

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It was reported in the preceding paper(1) that there exist two types of heterogeneous systems of acetic acid – ethyl ether – water (AEW), namely, the system which occasionally produces two types of emulsions (oil-in-water and water-in-oil) according to the two different modes of shaking, and the system which produces only one type of emulsion whatever the mode of shaking. Moreover, it was indicated the existence of a system which can behave both foamy and non foamy according to the two modes of shaking. Present paper describes the influence of the mode of shaking upon the type of emulsion and foam formation of the ternary heterogeneous system of acetic acid–benzene–water (ABW).

Experiments. In ABW-system, acetic acid is soluble in all proportions both in water and benzene, while benzene is insoluble in water. Mutual solubility diagram was obtained in the preceding paper(2) which is showin in Fig. 1. It covers a wide region of heterogeneous system.

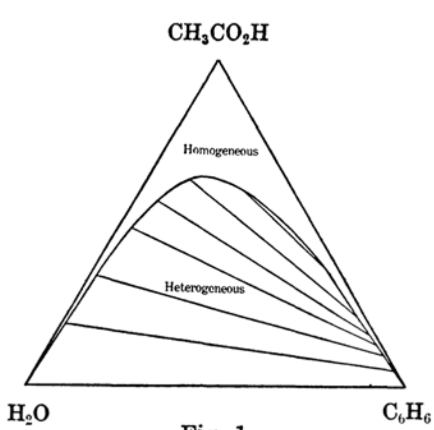


Fig. 1.

A definite volume (10 c.c.) of this heterogeneous system is taken in a test tube and the following two modes of shaking are applied.

(1) The test tube is held by hand vertically, pulled upwards quickly and then brought down slowly. After repeating these motions several times, usual up-and-down shaking is applied.

(2) The upper portion of the test tube is held by hand and the lower portion of it is swung repeatedly. Usual up-and-down shaking is subsequently applied.

The determination of the type of emulsion which is produced by above two modes of shaking is made by observing the process of breaking up of resulting emulsion in the following manner.(1) The emulsion is determined to be O-in-W type(3) when the droplets of disperse phase increase their size as they go upwards and a liquid layer is gradually separated

(1) Sasaki, this Bulletin, **14** (1939). 63.

(2) Sasaki, this Bulletin, **14** (1939), 3.

(3) O-in-Water represents emulsion in which the upper liquid layer of criginal heterogeneous system is dispersed in the lower one, and W-in-O represents the reverse type to O-in-W.

at the top from the bulk, while it is considered to be W-in-O type[3] when the droplets increase their size as they sink and a liquid layer is gradually separated at the bottom. Thus, in the various heterogeneous systems of ABW, the type of emulsion established by the above two modes of shaking were determined. Some of its data are shown in Table 1.

Table 1.

Composition in volume (c.c.)			Mode of shaking		Composition in volume (c.c.)			Mode of shaking	
Acetic acid	Benzene	Water	(1)	(2)	Acetic acid	Benzene	water	(1)	(2)
50.0	35.0	15.0	O-in-W	W-in-O	22.1	35.9	42.0	O-in-W	O-in-W
45.5	31.8	22.7	O-in-W	W-in-O	21.0	39.1	39 9	O-in-W	W-in-O
41.6	29.2	29.2	O-in-W	W-in-O	20.2	41.5	38.3	O-in-W	W-in-O
38.5	26.9	34.6	O-in-W	O-in-W	19.4	43.8	36.8	W-in-O	W-in-O
36.2	31.2	32.6	O-in-W	O-in-W	18.0	47.8	34.2	W-in-O	W-in-O
33.8	35.8	30.4	O-in-W	W-in-O	16.8	44.6	38.6	W-in-O	W-in-O
32.0	39 1	28.9	O-in-W	W-in-O	15.7	41.8	42.5	O-in-W	W-in-O
30.1	42.8	27.1	W-in-O	W-in-O	15.1	40.1	44.8	O-in-W	W-in-O
28.4	40.3	31.3	W-in-O	W-in-O	14.6	38.9	46.5	O-in-W	W-in-O
26.9	38.2	34.9	O-in-W	W-in-O	14.2	37.8	48.0	O-in-W	W-in-O
25.5	36.2	38.3	O-in-W	O-in-W	13.8	36 8	49.4	O-in-W	O-in-W
23.2	32.8	44.0	O-in-W	O-in-W					

It can be seen from this table that there exist two kinds of systems, that is, those systems which can produce only one type of emulsion independent of the modes of shaking, and those which occasionally produce both types of emulsion according to the different modes of shaking. In Fig. 2, A and B represent the region in which a system simply produces W-in-O or O-in-W emulsion respectively whatever the modes of shaking, and C represents the region in which a system shows the possibility of forming two types of emulsion, namely, it represents the phase inversion zone by shaking.

Precise investigations were further made upon the systems belonging to this phase inversion zone C. A definite volume (10 c.c.) of a system belonging to the phase inversion zone is taken and the following three modes of shaking are applied.

(1) The test tube is shaken as described in (1).
(2) The test tube is shaken as described in (2).
(3) The usual up-and-down shaking alone is applied from the beginning.

The usual up-and-down shaking involved in the above three modes of shaking is performed by the same shaking apparatus and on the same conditions (50 vibrations for 10 seconds with amplitude of 12 cm.) as described in the preceding paper.[4] The type of resulting emulsion is determined by observing the behaviour of breaking up of emulsion, in the same manner as described before. Following quantities were measured

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

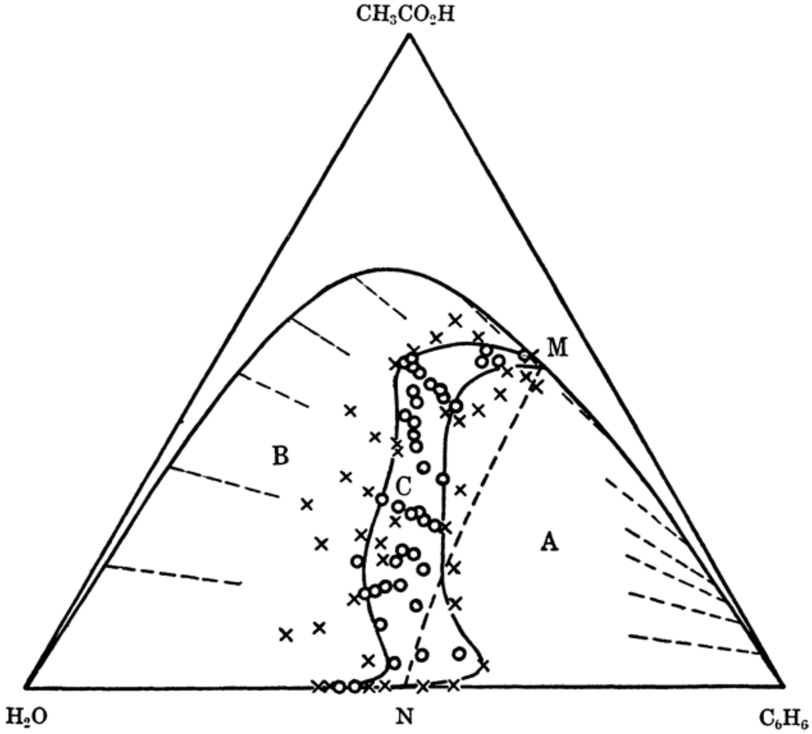


Fig. 2.

Table 2.

System	Compsition in volume (c.c.)			Mode of shaking			Volume ratio	
	Acetic acid	Benzene	Water	(1)	(2)	(3)	Upper layer	Lower layer
(a)	0.30	5.70	4.00	O-in-W $S_e = 104$ $S_f = 5$ $H = 0.8$	W-in-O $S_e = 26$ $S_f = 0$ $H = 0$	Same as in (2)	1.262	1.000
(b)	0.48	4.52	5.00	O-in-W $S_e = 112$ $S_f = 6$ $H = 0.8$	W-in-O $S_e = 25$ $S_f = 0$ $H = 0$	Same as in (1)	0.905	1.000
(c)	0.48	5.19	4.33	O-in-W $S_e = 130$ $S_f = 6$ $H = 1.0$	W-in-O $S_e = 27$ $S_f = 0$ $H = 0$	Same as in (1) and (2)	1.174	1.000
(d)	4.50	3.00	2 50	O-in-W $S_e = 29$ $S_f = 0$ $H = 0$	W-in-O $S_e = 21$ $S_f = 0$ $H = 0$	Same as in (1)	0.471	1 000

S_e and S_f denote stabilities of emulsion and foam respectively in second, and H represents height of foam in cm.

at the same time, that is, the stabilities of emulsion and foam which are denoted by time required from immediately after shaking to the complete collapse of foam zone and emulsion droplets respectively, the height of foam zone directly after the shaking, and the phase volume ratio. The results are shown in Table 2.

Discussion. It is evident in Fig. 2, that the heterogeneous region of ABW-system is divided into three portions A, B, and C, as in the case of AEW-system.[1] The region A mainly consists of systems having a larger volume of an upper layer (V_u) than that of a lower one (V_l). In such region a system shows tendency of the lower layer being dispersed in the upper one and becomes W-in-O emulsion, whatever the mode of shaking.[1] This tendency increases with difference in volumes between two layers, i.e., the system becomes W-in-O emulsion more easily as it approaches the mutual solubility curve. In region B, the relation is reverse. In the system of this region, V_u is smaller than V_l and so the system shows the tendency of the upper layer being dispersed in the lower one, that is, O-in-W emulsion results whatever the mode of shaking. This tendency also becomes more remarkable as the system approaches the mutual solubility curve.

Region A also involves systems in which V_l is a little larger than V_u, as was observed in the case of AEW-system.[1] In such systems, the lower layer having larger volume is dispersed in the upper one which cannot simply be explained by the above phase volume effect alone. It is rather the case in general that a ternary system shows such anomalies as in this case and in AEW-system.[1] Some other factors must be introduced, in addition to the above volume effect, to explain these phenomena. Specific action of interface was quoted for instance, in the preceding paper.[1]

Phase inversion zone C, namely, the region in which a system shows the tendency of producing both types of emulsion according to the different modes of shaking is situated between two regions A and B as shown in Fig. 2. The mode of shaking described in (1) favours to produce O-in-W emulsion, while the shaking of the mode (2) favours to produce W-in-O emulsion. Recently, the relation between emulsion type and mode of shaking was also indicated by Andreas[5] in the case of a system of immiscible triple layered liquid which is in accordance with our explanations.

The existence of the phase inversion zone was pointed out already in the preceding paper,[1] but the sharp boundary of this zone was not obtained in the case of AEW-system. In the present case, however, this zone is determined distinctly as shown in Fig. 2. The zone C is not situated along the dotted line MN in Fig. 2 which represents the locus of points corresponding to systems of V_u being equal to V_l. This is the case just similar to that of AEW-system. The position of phase inversion zone, therefore, cannot be determined by the volume ratio alone. It is however possible to say that in regions A and B, the effect of relative volume ratio is remarkable, while in phase inversion zone, the effect of modes of shaking as described in (1) and (2) are predominant in de-

(5) Andreas, *J. Chem. Education*, **15** (1938), 523.

termination of emulsion type. The influence of emulsifying agent is absent throughout in this system as in AEW-system.

In Table 2, three systems (a), (b) and (c) were all taken in the phase inversion zone C, so the shaking of the mode (1) or (2) favours to produce O-in-W or W-in-O emulsion respectively in these systems, on the same reason as was explained in the preceding paper.[1] In the present case, intermittent shaking described in (1) is especially effective[6] in producing O-in-W emulsion as it gives time to break relatively unstable W-in-O emulsion droplets produced simultaneously by shaking.

In the case of shaking of the mode (3) where the up-and-down shaking alone is applied from the beginning, these systems show difference in their behaviours. System (a) produces W-in-O emulsion, system (b) O-in-W emulsion and system (c) occasionally produces both types of them.

It was reported in the preceding paper[1] that in the phase inversion zone, those systems which are situated close to the region A show the tendency to produce emulsion of the similar type to that in region A (W-in-O) and those near the region B show the tendency of producing emulsion of the same type as that in region B (O-in-W). These facts were again confirmed in the present experiments. In Table 2, system (a) which is close to the region A, as shown in Fig. 3, has the tendency of producing emulsion of W-in-O type more easily than the other possible type of O-in-W emulsion on shaking. System (b), in the same manner, produces O-in-W emulsion more easily than that of W-in-O type. In the case of system (c), it is distant from both regions A and B, and it has equal tendency of producing both types of emulsions. All these three systems lie on a same tie-line, i.e., they consist of an upper and a lower layers of nearly one and the same composition respectively, and they merely differ in their volume ratio $V_u : V_l$. Above difference in behaviour of emulsion can therefore be ascribed mainly to the effect of volume ratio as shown in Table 2. It must be added that the system (c) which has equal tendencies of establishing both types of emulsions, is not always equally distant from two regions A and B, nor does it coincide with the middle point of a tie-line.

It happens frequently that the type of emulsion once established by a certain mode of shaking cannot be inverted by another mode of shaking, even in the phase inversion system. Thus in the system (b), O-in-W emulsion is relatively stable and simple up-and-down shaking produces emulsion of this type, but once W-in-O emulsion is established by the mode of shaking described in (1), subsequent up-and-down shaking merely favours to produce emulsion of the same type, instead of inverting it to another type. Sometimes, a certain mode of shaking which favours to produce one type of emulsion favours to accelerate the breaking-up of emulsion of another type which otherwise breaks up slowly. W-in-O emulsion of the system (c), for example, requires 130 seconds for the complete separation into two layers when it is left at rest after shaking. The time is reduced to about 84 seconds when it is shaken as described in (2). Such a phenomenon is similar to a demulsifying effect of one type of emulsify-

(6) Briggs, *J. Phys. Chem.*, **24** (1920), 120.

ing agent to emulsion which is stabilized by the emulsifying agent of another type, as indicated by Clowes.[7]

It was suggested in the preceding paper[1] that distinction must be made between the tendency to establish a type of emulsion and its stability, showing the example of AEW-system. The confirmation is further made in the case of ABW-system. It can be seen in Table 2, that the system (a) shows the tendency of producing W-in-O emulsion by the usual up-and-down shaking, although it is far more unstable than O-in-W emulsion.

The general difference in behaviour or appearance between O-in-W and W-in-O emulsions of ABW-system is summarised in Table 3. The

Table 3.

O-in-W emulsion	W-in-O emulsion
Produced by shaking of the mode (1)	Produced by shaking of the mode (2)
Emulsion drops increase their size as they go upwards and a liquid layer is separated upon the bulk. Relatively stable.	Emulsion drops increase their size as they sink and a liquid layer is separated at the bottom. Relatively unstable.
Emulsion is brilliant in light.	Emulsion is frosted and white.
Foamy or non foamy, triple layered foam[2] occurs frequently. Foamy emulsion is nearly silent on shaking.	Non foamy. Emulsion is noisy when shaken.
Air bubbles go upwards quickly with emulsion drops.	Air bubbles go upwards slowly between emulsion props.

nature of ABW-emulsion is somewhat different from that of AEW-emulsion. In ABW-system, O-in-W emulsion is more stable than W-in-O emulsion, while in AEW-system the latter is more stable than the former. It can be observed that heterogeneous system of ABW produces brilliant emulsion drops when O-in-W emulsion is formed on shaking. This is explained from the total refraction caused by emulsion drops which have smaller refractive index than that of dispersing medium. These behaviours can generally be observed in most other heterogeneous systems provided that there exists marked difference in refractive indices between two immiscible components. Emulsion is frosted and white in the case of W-in-O type. Emulsion usually makes noise on shaking, but it turns to be nearly silent when foam, acting as a cushion, is produced. Further, the motion of the air bubbles produced by shaking in the emulsion is also distinctive. In O-in-W emulsion the motion is quick, while in W-in-O emulsion it is slow as if the emulsion is fairly viscous.

Finally, it will be discussed upon the foam formation of ABW-emulsion. System (a), (b) and (c) foams when it is shaken by the mode (1), while it does not foam by shaking of the mode (2), as shown in Table 2. Existence of such a system has already been indicated in the preceding paper[1] for AEW-emulsion and was called foam-nonfoam system. The

(7) Clowes, *J. Phys. Chem.*, **20** (1916), 407.

effect of shaking upon foam-nonfoam system of ABW as described above is, however, just reverse to that of AEW in which foam is produced by shaking of the mode (2), while it is not produced by shaking of the mode (1).

It was concluded in the preceding paper(1) that the region of these foam-nonfoam systems is restricted in a portion of phase inversion zone which at the same time forms a part of foamy region of heterogeneous system. In Fig. 3, foamy region is expressed by B′(2) which is surrounded by a dotted line, and the phase inversion zone is also indicated by C. Hatched portion, therefore, corresponds to foam-nonfoam region of ABW-system. A system of this region foams when it produces O-in-W emulsion,

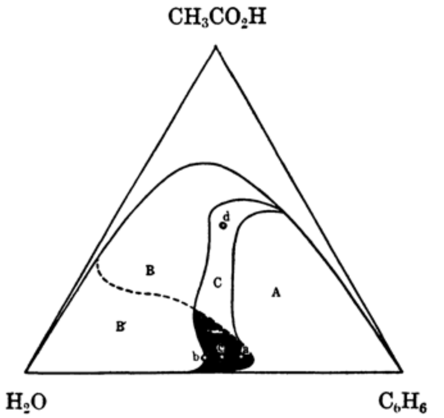
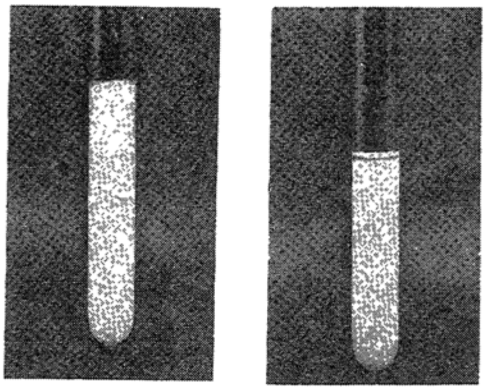


Fig. 3.



Foamy emulsion, produced by shaking of the mode (1).

Non foamy emulsion, produced by shaking of the mode (2).

Fig. 4.

for emulsion droplets having fairly smaller surface tension than the dispersing medium favour to produce triple layered foam.(2) It does not foam when it produces W-in-O emulsion like as the system of A region. Fig. 4 shows an example of such foam-nonfoam system.

The reverse effect of two modes of shakings to the foam formation between ABW- and AEW- systems can be explained by the fact that the foamy region of heterogeneous system is situated in B region (O-in-W region) in the case of ABW-system, while it is situated in A region (W-in-O region) in the case of AEW-system, and so the mode of shaking to produce foamy emulsion is different between two systems.

In the system (d) which is situated in phase inversion zone but not in the foamy region, emulsions of both types can be produced by shaking, but foam is not produced in either of them.

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Summary.

(1) The heterogeneous region of the system consisting of acetic acid, benzene and water (ABW) is divided into three regions A, B and C, referring to the type of emulsion produced by two different modes of shaking. Systems in region A or B produce water-in-oil or oil-in-water emulsion respectively, whatever the mode of shaking, and those in region C occasionally produce both types of emulsion according to the two modes of shaking. The region C is called the phase inversion zone by shaking.

(2) Some systems of this phase inversion zone behave both foamy and non foamy according to the two different modes of shaking. The existence of such foam-nonfoam system is restricted in a portion of the phase inversion zone which at the same time forms a portion of foamy region of heterogeneous system of ABW.

(3) The difference in nature or behaviour between two possible types of emulsions produced by one and the same system was compared in details, and its discussions were made.

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