On the Nature of Foam. IV. Phase Inversion and Foaming of Emulsion Consisting of Acetic Acid, Ethyl Ether and Water.

By Tunetaka SASAKI.

(Received February 10, 1939.)

It was reported in the preceding paper,(1) that the heterogeneous region of the system consisting of acetic acid, ethyl ether and water (AEW-system) is divided into two parts, namely, foamy and non foamy region. It was discovered, by a more detailed observation, that between these foamy and non foamy regions, there exist some system in which foam is produced by a certain mode of shaking, while it is not produced by another mode of shaking. Moreover, the type of emulsion is different in each of the above two cases. Present paper describes such phase inversion of AEW-emulsion produced by shakings and its influence upon the foam formation.

Experiments.

I. Foam-Nonfoam System.(2) We take a certain composition of AEW-system, for example, the system consisting of 2.33 c.c. of acetic acid, 3.79 c.c. of ethyl ether and 3.88 c.c. of water which corresponds to the point (a) in the mutual solubility diagram of AEW-system as shown in Fig. 1, and shake in a test tube. Then, the following two cases are observed according to two different modes of shaking.

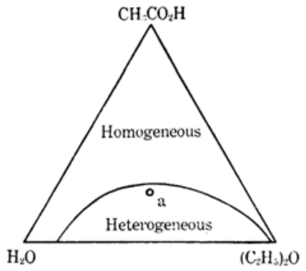


Fig. 1.

(1) The test tube is held vertically by hand, shaken up and down several times strongly in the usual manner, and then left at rest. In this case the formation of emulsion was observed without any indication of the foam formation.

(2) At first, the upper portion of the test tube is held and the lower portion is made to swing forwards and backwards until considerable amounts of upper and lower liquids are mixed together, then, the usual up-and-down shaking as in (1) is made and emulsification is completed. Observation after shaking shows the foam formation in the resulting emulsion.

II. Mode of Shaking and Emulsion Type. The results of section (I) show, that a certain system of AEW foams or does not foam according to the different modes of shaking. Such phenomena have not been observed up to the present. To investigate these phenomena more precisely, we have made close observations to the two emulsions obtained in (1) and (2) of section (I).

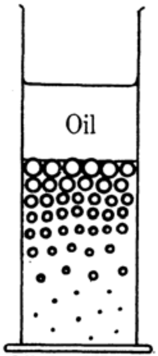
---

(1) Sasaki, this Bulletin, **13** (1938), 669.
(2) The term is used for such a system as shown in this section.

These emulsions are both unstable, their disperse phases consisting of comparatively large liquid drops. It may be called mechanical suspension rather than true emulsion. When we trace, however, the process of breaking up these two emulsions, following differences are observed between them.

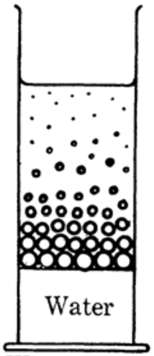
(1) In emulsion which is described in (1) of section (I), it can clearly be observed with naked eyes, that emulsion droplets move upwards in the dispersing medium increasing their size as they go up, and at the top of emulsion, in the course of time, they are separated from the dispersing medium as a transparent liquid layer upon the bulk. Thus, emulsion finally breaks up perfectly into two transparent liquid layers. Fig. 2 shows these behaviours.

(2) In emulsion which is described in (2) of section (I), the appearance is just reverse. Emulsion droplets sink in the dispersing medium, they grow in their size as they go down, and in the course of time they are separated, at the bottom, from the dispersing medium into transparent layer. The emulsion finally breaks up into two layers. These relations are also shown in Fig. 3.



Oil in Water

Fig. 2.



Water in Oil

Fig. 3.

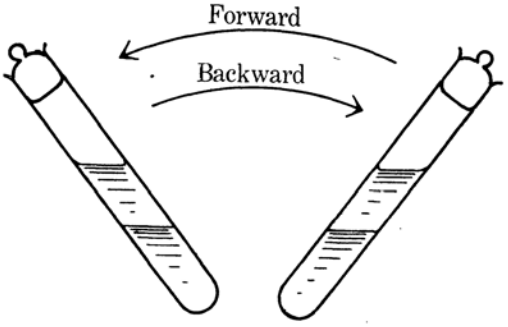


Fig. 4.

It is concluded from the above observations, that in the case of emulsion (1) or Fig. 2, the upper layer of original heterogeneous system is dispersed in the lower one. It may be called oil-in-water (O-in-W) emulsion, as the upper layer mainly consists of ethyl ether which is insoluble in the lower layer of aqueous mixture. In the case of emulsion (2) or Fig. 3, on the contrary, the lower layer of original system is dispersed in the upper one, or it may be called water-in-oil (W-in-O) emulsion. Thus, it is evident that in a certain composition of AEW-system, the mode of shaking described in (1) of section (I) favours the emulsification of oil in water which does not foam, while another mode of shaking as described in (2) of section (I) favours the emulsification of water in oil which foams. The foam formation of this system will be discussed later.

Further experiments show that the formation of O-in-W emulsion is still more facilitated by shaking a test tube in the following manner. The lower part of the test tube is held by hand and the upper portion is shaken with forward and backward motion, which is better described as a jerk. It is illustrated in Fig. 4,

III. Heterogeneous Region and Emulsion Type. As it is evident, that emulsion type is affected by the mode of shaking, we subsequently made experiments to examine how the type of emulsion of heterogeneous AEW-system is influenced by these two modes of shaking.

For this purpose, we take a constant volume of a system belonging to the heterogeneous region of AEW, and is shaken in a test tube by the following two manners.

(1) The test tube is shaken several times as shown in Fig. 4, and then, it is shaken up and down as in usual manner.

(2) The test tube is shaken in the same manner as described in (2) of section (I).

After shaking, the test tube is left at rest in vertical position, and the behaviour of breaking up of emulsion is observed. The following results have been obtained.

In the region where the volume of the upper layer is in excess compared with that of the lower one, emulsion is obtained in which the lower layer is dispersed in the upper one, i.e. W-in-O emulsion, no matter what the modes of shaking. Such a region is shown as A in Fig. 5. On the contrary, in the region where volume of the lower layer is in excess compared with that of the upper one, the upper layer is dispersed in the lower one, i.e. O-in-W emulsion is obtained, independent of the modes of shaking. This region corresponds to B in Fig. 5.

Now, between these A and B region, a narrow zone has been discovered in which a system changes its type of emulsion according to the above two modes of shaking. This is considered to be the zone of phase inversion by shaking. Observed systems belonging to this zone are shown in Table 1. These systems become O-in-W emulsion by the shaking of the mode (1), while they become W-in-O emulsion by the shaking of the mode (2). Plotting the points corresponding to these compositions on Fig. 5 (indicated by circlets), the line PQ is obtained. Although the shape of this phase inversion zone was not determined distinctly, it is considered to be a narrow region including the line PQ.

Table 1.

Volume composition of phase inversion system (c.c.)		
Acetic acid	Ethyl ether	Water
0	3.75	6.25
0.43	3.90	5.67
0.95	3.81	5.24
1.51	3.54	4.95
2.10	3.70	4.20
2.40	3.80	3.80

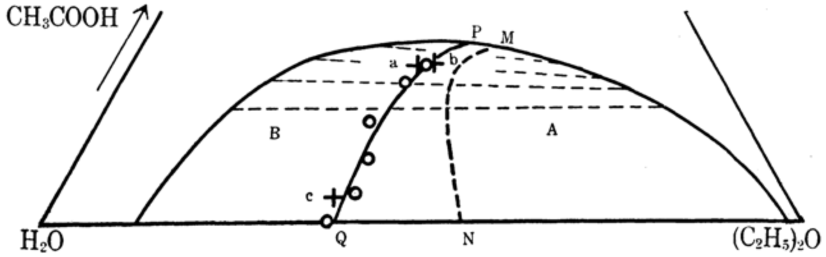


Fig. 5.

IV. Zone of Phase Inversion. In order to investigate this zone of phase inversion more precisely, we carried out, further, the following experiments.

We take systems belonging to this zone, namely, in the vicinity of the line PQ, and applied to them the following modes of shaking.

(1) The mode of shaking as shown in (1) of section (III) or the following method is employed which gives the same effect. The test tube is supported vertically, pulled upwards quickly and then brought down slowly. After repeating these motions several times, it is shaken up and down as in the usual manner.

(2) The mode of shaking as shown in (2) of section (III) is also adopted here.

(3) The test tube is simply shaken up and down as in the usual manner, from the beginning.

Up-and-down shaking involved in the above three modes of shaking is performed by the same shaking apparatus and in the same condition as described in the preceding paper⁽¹⁾ (50 vibrations for 10 seconds with amplitude of 12 cm.). Various quantities are measured for emulsion thus produced which are shown in Table 2. In this table, stability of emulsion or foam is expressed by time required from immediately after shaking to the complete collapse of emulsion droplets or foam zone, respectively. Height of foam zone is also measured soon after shaking.

Table 2.

System	Composition in volume (c.c.)			Mode of shaking			Volume ratio	
	Acetic acid	Ethyl ether	Water	(1)	(2)	(3)	Upper layer	Lower layer
(a)	2.33	3.79	3.88	O-in-W $S_e = 24$ $S_f = 0$ $H = 0$	W-in-O $S_e = 41$ $S_f = 1.5$ $H = 0\ 6$	O-in-W same as (1)	0.66	1.00
(b)	2.40	3.90	3.70	O-in-W $S_e = 28$ $S_f = 0$ $H = 0$	W-in-O $S_e = 44$ $S_f = 1.7$ $H = 0.5$	W-in-O same as (2)	0.72	1.00
(c)	0.38	3.66	5.96	O-in-W $S_e = 10$ $S_f = 0$ $H = 0$	W-in-O $S_e = 12.5$ $S_f = 0$ $H = 0$	O-in-W or W-in-O	0.45	1.00

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

V. Discussion. First of all, the experiments of section (I) show, that there exists a system of certain composition which can behave both foamy and non foamy, according to the modes of shaking. It is expected, that such difference in the foam formation is necessarily ascribed to the difference in the nature of emulsions in which these phenomena are taking place. In fact, it is confirmed, as described in section (II), that the foamy emulsion is W-in-O type (Fig. 3), while the non foamy emulsion is O-in-W one (Fig. 2). Thus, the phenomena of foam formation of such systems are closely related to the type of emulsion or the possibility of phase inversion which is caused especially by the mode of shaking.

Now. it is worth while to give a glance to the theories of type determination or phase inversion of emulsion.

The type of emulsion is generally considered to be determined by the nature of emulsifying agent. Bancroft(3) considered, that the interfacial tension between emulsifying agent and water or oil plays an important rôle and liquid which constitutes an interface of smaller interfacial tension forms a dispersing medium. Langmuir,(4) Harkins(4) and Hildebrand(4) indicated the relation between the type of emulsion and the molecular shape of emulsifying agent, which enables the explanation of the facts, that Na-soap favours the emulsification of O-in-W type, while Mg- or Al-soap favours that of W-in-O type. The phenomena of phase inversion are also influenced by above conditions. Clowes(5) succeeded to invert O-in-W emulsion stabilized by Na-oleate into W-in-O emulsion by adding Ca-salt to it. Bhatnagar(6) studied the effect of added electrolyte to the type or phase inversion of emulsion. Parsons and Wilson(7) also made the systematic investigation upon these lines.

Now, all these explanations assume the existence of the emulsifying agent of definite kind and its selective determination of type of emulsion. The emulsifying agent stabilizes one type of emulsion selectively to the opposite one. Above explanation, however, cannot be applied in the case where it is difficult to determine which of the liquid components is an emulsifying agent. It may be emphasized, that in these systems which belong to mechanical suspension rather than true emulsion, the readiness or tendency with which certain type of emulsion is produced, is the different matter from the stability of emulsion thus produced, as can be seen in the later part of this paper. Both of these factors are generally involved in all above theories and it is interesting to find the analogy between these relations and the suggestion made by Foulk(8) upon the mechanism of foam formation. The tendency of establishing either type of emulsion is sometimes confused with the stability. We, further, consider the cases where the effects of the other factors than the stability are predominant.

Briggs(9) noted, that a certain type of emulsion are quickly produced by the method of intermittent shaking. It is frequently experienced, that the emulsification is facilitated by adding the disperse phase little by little and not all at once. Wa. Ostwald(10) discussed the influence of volume ratio of two liquid components upon the type of emulsion and

---

(3) Bancroft, *J. Phys. Chem.*, **17** (1913), 501.

(4) Langmuir, *J. Am. Chem. Soc.*, **39** (1917), 1848; Harkins and co-workers, *ibid.*, **39** (1917), 354, 541; Finkle, Draper, and Hildebrand, *ibid.*, **45** (1923), 2780.

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

(6) Bhatnagar, *J. Chem. Soc.*, **117** (1920), 542; **119** (1921), 61, 1760.

(7) Parsons and Wilson, *Ind. Eng. Chem.*. **13** (1921), 1116.

(8) Foulk, *Ind. Eng. Chem.*, **21** (1929), 815.

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

(10) Wa. Ostwald, *Kolloid-Z.*, **6** (1910), 103.

indicated the critical volume ratio at which the system undergoes phase inversion. Robertson⁽¹¹⁾ and Bhatnagar⁽⁶⁾ also observed the same effect. Ostwald⁽¹⁰⁾ further pointed out another possibility, that the emulsion type is determined by the influence depending upon whether the glass surface of the vessel is wetted with oil or water previous to making emulsion and said, that in certain system of two liquids, the poorer wetting liquid will be emulsified in the better one. Although these factors are overshadowed in its determining effect by the nature of the emulsifying agent, as discussed by Briggs and Schmidt,⁽¹²⁾ they have considerable effects in the case of unstable and coarser mechanical suspensions with no emulsifying agent specified.⁽⁶⁾ These factors rather affect the process of establishment of emulsion type, and not the stability of emulsion produced. The mode of shaking discussed in this paper is also considered to be one of these factors where the emulsifying agent has little significance.

It is described in section (III), that the heterogeneous region of AEW-system is divided into three parts, referring to the type of emulsion, as shown in Fig. 5. The region A of this diagram mainly consists of systems having fairly larger volume of an upper layer (V_u) than that of a lower one (V_l). Such a system shows the tendency of the lower layer being dispersed in the upper one, namely, W-in-O emulsion, no matter what the mode of shaking. This tendency seems to be determined mainly by the ratio $V_u:V_l$ as suggested by Bhatnagar⁽⁶⁾ and Robertson,⁽¹¹⁾ namely, in case where there is marked difference in volume between two layers, liquid of larger volume shows the tendency of becoming a dispersing medium, and this tendency is more remarkable as the difference in volume grows larger. In the region B, the relation is reverse. Here V_l is markedly larger than V_u, and the system of this region shows the tendency of the upper layer being dispersed in the lower one, namely, O-in-W emulsion results, independent of the mode of shaking.

It is interesting to note, that the region A contains a system in which V_u is smaller than V_l and yet the upper layer becomes a dispersing medium on shaking. This suggests that some other factors, in addition to volume ratio, influence the tendency in establishing an emulsion type. Specific action of interface, for example, can be considered.

Phase inversion zone, namely, the region in which a system shows the tendency of producing both types of emulsions according to the mode of shaking, is situated along PQ line in Fig. 5. Such possibility of forming two types of emulsions from one and the same system was once pointed out by Ostwald.⁽¹⁰⁾ Woodman⁽¹³⁾ studied the system of cresylic acid–gelatine–water, and observed that, in certain case, both types of emulsions are possible, depending mainly upon the mode of shaking. The fact was confirmed distinctly in the present experiments.

When we trace the locus of middle points of tie-lines (i.e. points corresponding to the system in which $V_u = V_l$), dotted line MN is obtained in Fig. 5. Now, if the emulsion type is determined by the volume ratio

---

(11) Robertson, *Kolloid-Z.*, **7** (1910), 7.

(12) Briggs and Schmidt, *J. Phys. Chem.*, **19** (1915), 478.

(13) Woodman, *J. Phys. Chem.*, **30** (1926), 658.

of two liquids alone, phase inversion zone is reduced to the line PQ which must coincide to the line MN. In practice, phase inversion zone has a narrow area instead of a line, and does not coincide to the line MN which is situated in the region A, as shown in Fig. 5. This means, that the position of the phase inversion zone cannot be determined by volume ratio alone, and also indicates the influences of some other factors. The specific action, at the interface, of acetic acid is quoted for example. It is clear, that in regions A and B, the influence of relative volume ratio is remarkable, while in phase inversion zone, the effect of the mode of shaking is predominant in determination of emulsion type.

Now, we are confronted to the explanation of the mechanisms of shaking. Woodman,(13) in his experiments, attempted the explanation which, however, is complicated because adsorption, aging and partition between two phases of an emulsifying agent (gelatine) must be taken into account. In the present case, however, such disturbing factors due to the emulsifying agent are absent and mechanisms seem to be more simple.

In the case of shaking described in (1) of section (III), the lower part of a test tube is fixed and the upper portion of it is swung. Accordingly, the upper layer in the tube is first thrown against the upper end of the tube by the action of centrifugal force, and then follows the lower layer. Thus, the upper layer is crushed into droplets by compression between wall and the lower layer in which it is dispersed. Repeated shaking in this manner, therefore, establishes O-in-W emulsion and subsequent ordinary shaking of up-and-down motion also favours to increase the degree of dispersion of above emulsion type. The mode of shaking described in later part of (1) of section (IV) can be considered to give the same effect as the above case.

In the case of shaking mentioned in (2) of section (III), the upper portion of the tube is fixed and the lower portion is made to swing. In this case, the lower layer is not stirred, as it is confined between the upper layer and wall of the tube, while the upper layer is agitated, especially strong at the free surface. The agitation is extended down to the interface of two layers, where the lower liquid is stirred up and is gradually dispersed into the upper one. W-in-O emulsion is, therefore, established as the shaking goes on, and subsequnt ordinary up-and-down shaking also increases the degree of dispersion of this emulsion type.

The question arises as to what type would the ordinary up-and-down shaking favour to produce when it is applied from the beginning. It will be discussed upon this point.

In Table 2, three systems, (a), (b) and (c) are all taken in the phase inversion zone, and so the mode of shaking described in (1) or (2) of section (IV) favours to produce O-in-W or W-in-O emulsion respectively, in these systems. In the case, however, where usual up-and-down shaking is applied from the beginning as described in (3) of section (IV), system (a) produces O-in-W emulsion, system (b) that of W-in-O type, and system (c) occasionally produces both types of them. Each of these emulsion types is considered to be more favourable, respectively, than the other possible type. In phase inversion zone, those systems which are situated near the region A, generally show the tendency to produce emulsion of the similar type to that in the region A (W-in-O emulsion as in (b)), and those near the region B show the tendency of producing emulsion of the same type as that in the region B (O-in-W emulsion as in (a)), by up-and-down shaking. Between these systems of (a) and (b), it is possible to consider the existence of such a system as (c), namely, the system which occasionally shows the tendency to produce both types of emulsions by up-and-down shaking.

It can also be seen from this table, that the type of emulsion once determined by a certain mode of shaking, is hard to be invrted by another mode of shaking. For example, system (b) produces W-in-O emulsion by usual up-and-down shaking, but when O-in-W emulsion is once established by the mode of shaking described in (1) of section (IV), subsequent up-and-down shaking only favours to increase the degree of dispersion of O-in-W type.

It is suggested in the earlier part of this section, that the distinction must be made between the tendency in establishment of emulsion type and the stability. Now, confirmations are made upon this point in Table 2. In the system (a), O-in-W emulsion is favourable to be produced in preference to W-in-O emulsion by usual mode of shaking, although emulsion of the latter type once produced is far more stable than that of the former, as shown in Table 2.

The general differences in behaviour or appearance between O-in-W and W-in-O emulsions are summarised in Table 3. It is said,(14) that there exists difference in stability between two possible types of drops formed at the interface separating two liquids. The present experiment shows it quantitatively.

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 drop moves upwards. Oily layer is separated upon the bulk (Fig. 2). Emulsion is comparatively unstable.	Emulsion drop sinks. Aqueous layer is separated at the bottom (Fig. 3). Emulsion is comparatively stable.
System does not foam. Bubble-in-drop system occurs frequently.	Foamy system occurs frequently.

Last of all, the explanation must be made upon the foam formation of the system shown in section (I). It is called for convenience sake foam-nonfoam system. Existence of such system is restricted in the region which forms a portion of phase inversion zone and at the same time forms a portion of foamy region of heterogeneous system of AEW.

---

(14) Rehbinder and Wenström, *Kolloid-Z.*, **53** (1930), 145.

In Fig. 6, A′ surrounded by dotted line, shows the foamy region⁽¹⁾ and hatching indicates the region of foam-nonfoam system.

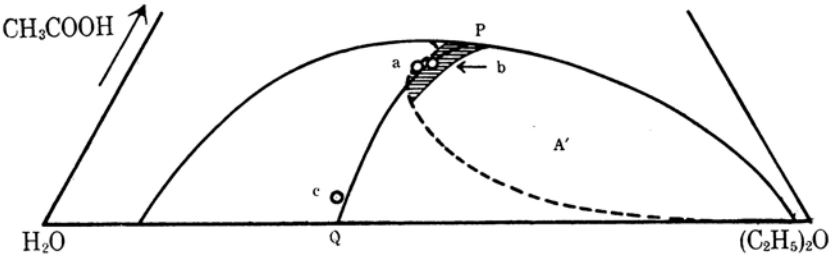


Fig. 6.

When we shake a system belonging to this region (system (a) or (b)), both types of emulsions are occasionally produced. In the case of O-in-W emulsion, bubbles which are produced at the same time in aqueous medium by shaking, are destroyed by emulsion droplets having smaller surface tension than that of dispersing medium, and no foam can be produced. In the case of W-in-O emulsion, on the other hand, emulsion droplets having larger surface tension than that of dispersing medium neither break bubbles, nor interfere with the foam formation of the system. These behaviours were schematically explained in the preceding report.⁽¹⁾ Accordingly, the above systems do not foam by shaking of the mode (1), while they can foam by shaking of the mode (2) of section (IV).

In the case of the system (c), the conditions are different. This system also belongs to phase inversion zone, but it is distant from the foamy region A′. So the system does not foam even when it forms W-in-O emulsion by shaking of the mode (2), while it produces emulsion droplets containing air bubbles, when it forms O-in-W emulsion by shaking of the mode (1) of section (IV), owing to the marked difference in surface tension between two phases.⁽¹⁾

In foam-nonfoam system, therefore, the emulsion type is most readily confirmed by the presence or absence of the foam formation immediately after shaking. If the type of emulsion is inverted by some accident during the shaking, sharp change in foam formation can be observed. Thus, in a foam-nonfoam system which shows strong tendency to establish non foamy emulsion, foam formation can be seen so far as it is carefully shaken by the mode (2). It, however, turns suddenly into non foamy system, when it is shaken too strongly.

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 from a grant given to Prof. Sameshima by Nippon Gakujutsu Shinkokwai) (Japan Society for the Promotion of Scientific Research), to which the author's thanks are due.

Summary.

(1) It has been discovered, that there is certain heterogeneous system consisting of acetic acid, ethyl ether and water, which behaves

both foamy and non foamy, according to the different modes of shaking. This behaviour in foam formation is due to the difference in the type of emulsions produced.

(2) Three modes of shaking were noted and their influences upon the type of emulsion have been discussed.

(3) The heterogeneous region of this system is divided into three parts, according to the type of emulsion produced by shaking, namely, oil-in-water region, water-in-oil region and phase inversion zone. In phase inversion zone, both types of emulsions are possible to be produced by different modes of shaking. Observations and discussions were made upon these emulsions.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.