# On the Nature of Foam. VI. Emulsion and Foam Formation of Ternary System, Ethyl Alcohol—Ethyl Ether—Water.

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It was indicated in the preceding papers⑴⑵ that in ternary systems of acetic acid–ethyl ether–water (AEW) and acetic acid–benzene–water (ABW), the diagram showing the relation between foam formation and composition has two maxima, one of which being situated in the region where the system shows critical opalescence or anomalous viscosity. In the case of ternary system of ethyl alcohol–ethyl ether–water (EEW), however, it has been known that there exists no region of such critical opalescence.⑶ It is interesting, therefore, to investigate whether this system has or lacks the maximum of foam formation corresponding to the absence of critical opalescence. Present paper describes the foam formation and the nature of emulsion of EEW-system.

**Experiments.** In ternary system of EEW, ethyl alcohol is soluble in all proportions both in ether and in water, while ethyl ether is hardly miscible with water. The mutual solubility curve of this system was obtained by the measurements of volume compositions of limiting turbid mixtures.⑴ The data and the diagram are shown in Table 1 and in Fig. 1. Tie-lines were determined from a volume ratio of upper and lower

Table 1.

| Volume composition of limiting turbid mixture (c.c.) | | |
|---|---|---|
| Ethyl alcohol | Ethyl ether | Water |
| 0 | 1.15 | 8.85 |
| 0 | 9.80 | 0.20 |
| 1.45 | 1.30 | 7.25 |
| 1.55 | 7.75 | 0.70 |
| 2.40 | 1.59 | 6.01 |
| 2.45 | 6.12 | 1.43 |
| 2.52 | 5.90 | 1.58 |
| 2.81 | 2.52 | 4.67 |
| 2.81 | 4.93 | 2.26 |
| 2.88 | 3.52 | 3.60 |
| 2.92 | 3.66 | 3.42 |

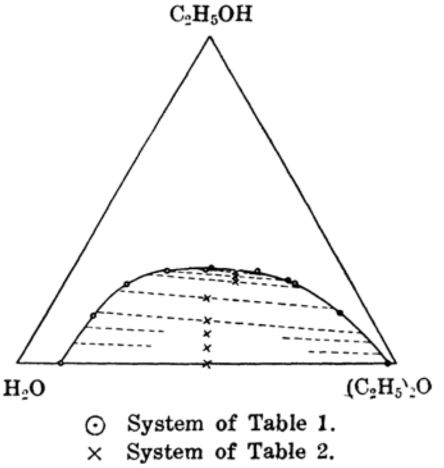

Fig. 1.

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(1) Sasaki, this Bulletin, **13** (1938), 669.
(2) Sasaki, this Bulletin, **14** (1939), 3.
(3) Sata and Kimura, this Bulletin, **10** (1935), 409.

liquid layers ($V_u$ and $V_l$ respectively) coexisting in a heterogeneous system, as described in the preceding paper.⁽¹⁾ The data are shown in Table 2 and are also depicted in Fig. 1.

Table 2.

| Composition in volume (c.c.) | | | Volume ratio | |
|---|---|---|---|---|
| Ethyl alcohol | Ethyl ether | Water | Upper layer | Lower layer |
| 0 | 5.00 | 5.00 | 0.818 | 1.000 |
| 0.48 | 4.76 | 4.76 | 0.763 | 1.000 |
| 0.90 | 4.55 | 4.55 | 0.742 | 1.000 |
| 1.30 | 4.35 | 4.35 | 0.707 | 1.000 |
| 2.00 | 4.00 | 4.00 | 0.700 | 1.000 |
| 2.50 | 4.50 | 3.00 | 1.334 | 1.000 |
| 2.65 | 4.41 | 2.94 | 1.390 | 1.000 |
| 2.79 | 4.33 | 2.88 | 1.630 | 1.000 |

The measurements of the foam stability were then undertaken for homogeneous and heterogeneous systems of EEW, using the same shaking apparatus and on the same conditions as described in the preceding paper.⁽¹⁾ A constant volume (10 c.c.) of liquid for measurement is introduced in a test tube of 1.5 cm. in diameter and 15 cm. in length, and is shaken 300 times for 10 seconds with amplitude of 12 cm. The time required from immediately after the stop of shaking to the complete collapse of foam zone was measured and was considered to be the stability of foam. The height of foam was not measured for the sake of simplicity. Some of the results of measurements are shown in Table 3, the data of which are shown diagramatically in Fig. 2.

Table 3.

| Composition in volume (c c.) | | | Stability of foam (second) | Composition in volume (c.c.) | | | Stability of foam (second) |
|---|---|---|---|---|---|---|---|
| Ethyl alcohol | Ethyl ether | Water | | Ethyl alcohol | Ethyl ether | Water | |
| 0 | 1.15 | 8.85 | 0 | 2.60 | 3.70 | 3.70 | 1.3 |
| 0 | 9.80 | 0.20 | 0 | 2.70 | 3.10 | 4.20 | 0 |
| 0.25 | 0 | 9.75 | 6.1 | 2.86 | 2.80 | 4.34 | 0 |
| 0.50 | 0 | 9.50 | 7.3 | 2.90 | 3.40 | 3.70 | 1.8 |
| 0.50 | 0.50 | 9.00 | 2.2 | 2.90 | 3.70 | 3.40 | 0 |
| 0.50 | 1.00 | 8.50 | 1.7 | 2.90 | 5.10 | 2.00 | 3.1 |
| 0.98 | 1.22 | 7.80 | 1.8 | 3.00 | 2.00 | 5.00 | 10.6 |
| 1.00 | 0.50 | 8.50 | 4.6 | 3.00 | 2.50 | 4.50 | 17.9 |
| 1.20 | 5.80 | 3.00 | 0 | 3.00 | 3.00 | 4.00 | 36.9 |
| 1.50 | 0 | 8.50 | 3.9 | 3.00 | 3.50 | 3.50 | 22.4 |
| 1.50 | 1.00 | 7.50 | 1.8 | 3.00 | 4.00 | 3.00 | 22.2 |
| 1.50 | 7.00 | 1.50 | 1.2 | 3.00 | 4.50 | 2.50 | 6.8 |
| 1.90 | 1.40 | 6.70 | 0 | 3.50 | 0 | 6.50 | 2.6 |
| 2.00 | 0.50 | 7.50 | 2.3 | 3.50 | 3.00 | 3.50 | 4.2 |
| 2.00 | 1.00 | 7.00 | 8.9 | 3.50 | 3.80 | 2.70 | 3.0 |
| 2.00 | 5.50 | 2.50 | 1.4 | 4.00 | 1.00 | 5.00 | 2.6 |
| 2.20 | 3.90 | 3.90 | 0.5 | 4.50 | 3.00 | 2.50 | 1.5 |
| 2.50 | 1.00 | 6.50 | 2.9 | 5.00 | 5.00 | 0 | 0 |
| 2.50 | 4.50 | 3.00 | 1.7 | 6.00 | 2.00 | 2.00 | 0.5 |
| 2.50 | 6.00 | 1.50 | 2.6 | 7.50 | 2.50 | 0 | 0 |
| 2.50 | 7.50 | 0 | 0 | | | | |

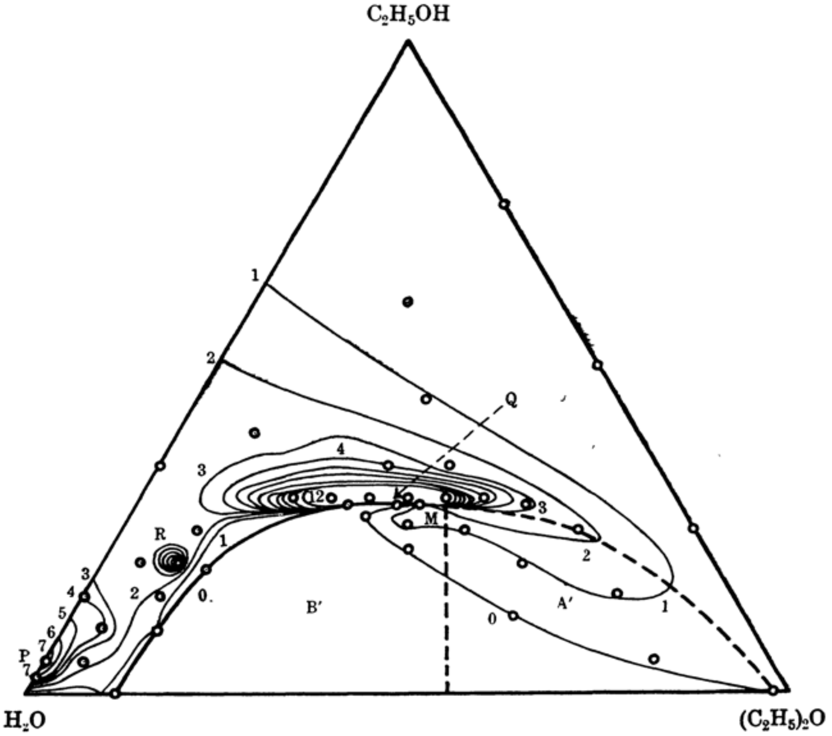

Fig. 2.

An emulsion produced by a system belonging to the heterogeneous region of EEW also exhibits characteristic behaviours according to the different modes of shaking as described in the preceding papers.(4)(5) So it was further investigated precisely. 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 to it.

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

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

The type of emulsion thus produced is determined by the appearance of breaking up of emulsion as shown in the preceding paper,(4) namely, emulsion is considered to be oil in water (O-in-W) type when drops of disperse phase increase their size as they go upwards and gradually separate themselves as a liquid layer upon the bulk, while it is considered to be water in oil (W-in-O) type when drops of disperse phase increase their size as they sink and gradually separate themselves as a liquid layer at the bottom. Thus, the type of emulsion produced in various heterogeneous systems of EEW were determined. Some of the

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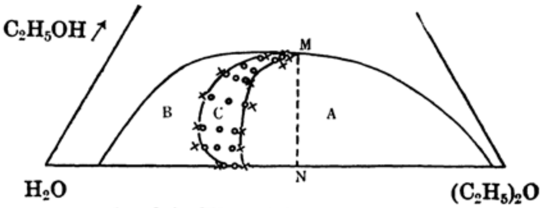
(4) Sasaki, this Bulletin, **14** (1939), 63.
(5) Sasaki, this Bulletin, **14** (1939), 107.

Table 4.

| Composition in volume (c.c.) | | | Type of emulsion produced by shaking of the mode | |
|---|---|---|---|---|
| Ethyl alcohol | Ethyl ether | Water | (1) | (2) |
| 2.90 | 3.70 | 3.40 | O-in-W | O-in-W |
| 2.80 | 3.40 | 3.80 | O-in-W | O-in-W |
| 2.79 | 3.75 | 3.46 | O-in-W | W-in-O |
| 2.75 | 3.30 | 3.95 | O-in-W | W-in-O |
| 2.71 | 3.93 | 3.36 | W-in-O | W-in-O |
| 2.70 | 3.65 | 3.65 | O-in-W | W-in-O |
| 2.59 | 3.89 | 3.52 | W-in-O | W-in-O |
| 2.55 | 3.04 | 4.41 | O-in-W | W-in-O |
| 2.45 | 3.30 | 4.25 | O-in-W | W-in-O |
| 2.40 | 2.60 | 5.00 | O-in-W | O-in-W |
| 2.35 | 2.75 | 4.90 | O-in-W | W-in-O |
| 2.18 | 3.27 | 4.55 | O-in-W | W-in-O |
| 2.14 | 3.39 | 4.47 | W-in-O | W-in-O |
| 1.80 | 2.50 | 5.70 | O-in-W | O-in-W |
| 1.75 | 2.72 | 5.53 | O-in-W | W-in-O |
| 1.54 | 3.59 | 4.87 | O-in-W | W-in-O |
| 1.50 | 3.75 | 4.75 | W-in-O | W-in-O |
| 1.00 | 2.80 | 6.20 | O-in-W | O-in-W |
| 0.98 | 2.94 | 6.08 | O-in-W | W-in-O |
| 0.88 | 3 68 | 5.44 | O-in-W | W-in-O |
| 0.86 | 3.84 | 5.30 | W-in-O | W-in-O |
| 0.50 | 3.00 | 6.50 | O-in-W | O-in-W |
| 0.48 | 3.27 | 6.25 | O-in-W | W-in-O |
| 0.44 | 3.86 | 5.70 | O-in-W | W-in-O |
| 0.43 | 4.02 | 5.55 | W-in-O | W-in O |
| 0 | 4.35 | 5.65 | W-in-O | W-in-O |
| 0 | 4.12 | 5.88 | C-type* | W-in-O |
| 0 | 3.86 | 6.14 | C-type* | W-in-O |
| 0 | 3.75 | 6.25 | O-in-W | O-in-W |

* Complex type i.e. the upper layer is W-in-O type and the lower layer, O-in-W type.

results are shown in Table 4. These data are depicted in Fig. 3. In this figure, A and B represent the region in which systems show only one type of emulsion, W-in-O and O-in-W types respectively, whatever the modes of shaking, and C represents the region in which systems show the tendency to produce both types of emulsions according to the above two modes of shaking.



○ O-in-W or W-in-O system.
× Phase inversion system.

Fig. 3.

In the phase inversion zone, a series of systems, varying in volume ratio of upper and lower liquid layers of nearly definite compositions respectively, were investigated in order to see the effect of volume to the nature of emulsion produced by shaking. In this measurements, 10 c.c. of a system is taken in a test tube and the following three modes of shaking are applied to it.

(1) The mode of shaking described in (1) of Table 4.
(2) The mode of shaking described in (2) of Table 4.
(3) Usual up-and-down shaking only is applied from the beginning.

The type of emulsion produced by above three modes of shaking are determined from the behaviours of breaking up of emulsion in the same manner as described before. The stability of emulsion, that is, the time required from immediately after shaking to the complete collapse of emulsion droplets, was also measured. The results are shown in Table 5.

**Discussion.** The diagram of the foam stability of EEW-system, as a whole, is similar in the shape to that of ABW-(2) and especially to AEW-system.(1) In the homogeneous region, surface of the diagram is steep along ethyl alcohol–water line and particularly the steepest along a portion of mutual solubility curve, while it has a gentle slope towards ethyl ether–ethyl alcohol line. The stability of foam shows maxima at three points P, Q and R in Fig. 2. Point P corresponds to the maxima of foam stability of binary mixture, ethyl alcohol–water, which has already been determined from the measurement of foam stability by another method.(6) The maximum point Q is situated along the mutual solubility curve and the degree of stability at this point far more exceeds that at P. These relations are quite similar to AEW-system.(1)

It was suggested in AEW-(1) and especially in ABW-system(2) that such region of remarkable foam stability and the region of critical opalescence or anomalous viscosity take the same position. Such regions are also near the point of intersection (M in Fig. 2) made by the mutual solubility curve and the locus of middle points of tie-lines. In the heterogeneous system near this point, the physical properties of upper and lower liquid layers closely resemble each other and the system shows the nature of colloidal solution when shaken. The maximum of foam formation as well as critical opalescence and anomalous viscosity was explained from this colloidal nature in the preceding papers.(1)(2) In the present case of EEW-system, the foam stability shows its maximum at point Q, although it is known that critical opalescence is absent in this system.(3) The point Q is also situated in the vicinity of the point of intersection (M) made by the mutual solubility curve and the locus of middle points of tie-lines. Maximum of foam stability can also be seen at point R, but it is rather uncertain as the vicinity of this point was not precisely investigated.

The diagram of foam stability in the heterogeneous region of EEW-system, like that of AEW-system, consists of two parts, foamy and non foamy regions which are represented as A′ and B′, respectively, in Fig. 2.

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

In a heterogeneous system of A′ region, foam can be produced on shaking, because a lower liquid layer of larger surface tension and smaller volume is dispersed in an upper one, and the foam formation was not prevented by these emulsion drops as was described in the preceding paper.(1) In a heterogeneous system of B′ region, an upper liquid layer of smaller surface tension and smaller volume is dispersed in a lower one on shaking.(1) In such conditions, the film of foam is destroyed by emulsion droplets and the system does not foam on shaking. Frequently, emulsion droplets containing air bubbles are obtained on shaking in the case where emulsion droplets have considerably smaller surface tension than the dispersing medium as in the case of AEW-system.

The heterogeneous region is divided into three portions A, B and C, referring to the type of emulsion produced by shaking as shown in Fig. 3. In a heterogeneous system of A region, the upper liquid layer is generally excessive in volume compared with the lower one and the system shows the tendency of the lower layer being dispersed in the upper one, namely, W-in-O emulsion results whatever the modes of shaking.(4) A heterogeneous system of B region, in the same manner, shows the tendency of the upper layer being dispersed in the lower one and O-in-W emulsion results, independent of the modes of shaking. The region A also involves systems in which a lower layer is slightly excessive in volume than the upper one, and yet the former is dispersed in the latter. The system of C region shows the tendency of producing both types of emulsion according to the two different modes of shaking. The modes of shaking described in (1) favours to produce O-in-W emulsion and the shaking of the mode (2) favours to produce W-in-O emulsion. These relations between mode of shaking and type of resulting emulsion is similar to those of AEW- and ABW-systems, and they can also be explained in the same manner.(4) The region C is also called the zone of phase inversion by shaking. It can be seen that this zone of phase inversion is not situated along the line MN. It is not necessary for the phase inversion system that volumes of upper and lower layers are equal, as in the case of AEW-(4) and ABW-systems.(5) The behaviours of a system belonging to the zone of phase inversion was precisely studied and are tabulated in Table 5. It can be seen in this table that the behaviours of phase inversion systems to the shaking gradually change with relative volume ratio of coexisting upper and lower liquid layers.

The phase inversion system (a) which has relatively smaller value of $V_u/V_l$, namely, which is situated close to the region B, shows a strong tendency to become O-in-W emulsion by shaking of the modes (1) and (3). W-in-O emulsion which is produced only by careful shaking of the mode (2), readily turns to O-in-W emulsion by a slight up-and-down shaking. In system (b) and (c) which have a little larger value of $V_u/V_l$ than that of the system (a), O-in-W emulsion becomes also selectively produced by the usual up-and-down shaking of the mode (3) as in the system (a), but the tendency to produce W-in-O is more remarkable in (b) and (c) than in (a). W-in-O emulsion produced in the systems (b) and (c) by shaking of the mode (2) can be inverted to O-in-W emulsion only by a strong shaking. This tendency is even more conspicuous in the system (d). In this system, both types of emulsion once established by shakings of the modes (1) and (2) cannot be inverted each other, even by a violent shaking. In the system (d), however, there is still difference between the tendency of producing O-in-W emulsion and that of W-in-O emulsion. Emulsion of the former type is selectively produced by the usual up-and-down shaking. The tendency of producing W-in-O emulsion becomes still more marked until, at last, in system (e) and (f) which have more higher values of $V_u/V_l$ than that of (d), the tendencies of producing both types of emulsions become equal. In such systems, two possible types of emulsions produced by shaking of the modes (1) and (2) cannot of course be inverted each other by any shaking. Moreover, usual up-and-down shaking occasionally produces both types of emulsions. Thus, in systems (e) and (f), two types of emulsions are utterly equal in their tendencies of formation on shaking. These system are, therefore, considered to be the true intermediate or boundary systems between W-in-O and O-in-W regions (A and B regions), but it is not necessary that these systems should be equally distant from both of these regions. The tendency of producing W-in-O emulsion overcomes that of O-in-W emulsion as we go further from (f) to (i) (namely, as a system approaches A region), and the emulsion of the former type is selectively

Table 5.

| System | Composition in volume (c.c.) | | | Volume ratio | | Type and stability of emulsion produced by shaking of the mode | | |
|---|---|---|---|---|---|---|---|---|
| | Ethyl alcohol | Ethyl ether | Water | Upper layer | Lower layer | (1) | (2) | (3) |
| (a) | 1.50 | 2.70 | 5.80 | 0.259 | 1.000 | O-in-W $\leftleftarrows$<br>$S_e = 8$ | W-in-O<br>$S_e = 10$ | O-in-W |
| (b) | 1.50 | 2.80 | 5.70 | 0.293 | 1.000 | O-in-W $\longleftarrow$<br>$S_e = 8$ | W-in-O<br>$S_e = 11$ | O-in-W |
| (c) | 1.50 | 3.00 | 5.50 | 0.348 | 1.000 | O-in-W $\longleftarrow$<br>$S_e = 8$ | W-in-O<br>$S_e = 12$ | O-in-W |
| (d) | 1.50 | 3.10 | 5.40 | 0.372 | 1.000 | O-in-W ←×→<br>$S_e = 9$ | W-in-O<br>$S_e = 14$ | O-in-W |
| (e) | 1.50 | 3.20 | 5.30 | 0.380 | 1.000 | O-in-W ←×→<br>$S_e = 7$ | W-in-O<br>$S_e = 12$ | both types |
| (f) | 1.50 | 3.30 | 5.20 | 0.400 | 1.000 | O-in-W ←×→<br>$S_e = 8$ | W-in-O<br>$S_e = 14$ | both types |
| (g) | 1.50 | 3.40 | 5.10 | 0.448 | 1.000 | O-in-W ←×→<br>$S_e = 10$ | W-in-O<br>$S_e = 15$ | W-in-O |
| (h) | 1.50 | 3.45 | 5.05 | 0.470 | 1.000 | O-in-W ←×→<br>$S_e = 10$ | W-in-O<br>$S_e = 16$ | W-in-O |
| (i) | 1.50 | 3.50 | 5.00 | 0.485 | 1.000 | O-in-W $\longrightarrow$<br>$S_e = 9$ | W-in-O<br>$S_e = 15$ | W-in-O |

$S_e$ denotes the stability of emulsion in second.
$\leftleftarrows$ inversion with ease by shaking of the mode (3).
$\longleftarrow$ inversion with difficulty.
←×→ no inversion.

established by up-and-down shaking. The tendency of inversion from O-in-W to W-in-O also increases as the system approaches the region A. These relations can be seen in Table 5 and in Fig. 4.

In the heterogeneous binary system of ethyl ether and water, phase inversion by shaking does not occur, but some systems exhibit complex dispersion, producing both types of emulsions simultaneouly by shaking.

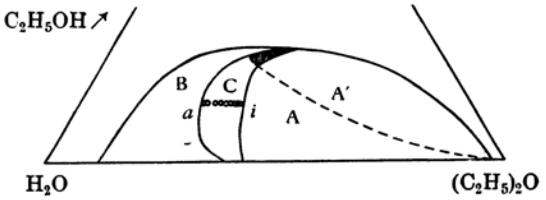

Fig. 4.

It can also be pointed out that the stability of emulsion ($S_e$) is not always parallel to its tendency of formation.(4) In Table 4, W-in-O emulsion is more stable than O-in-W emulsion throughout all systems of phase inversion zone, but in systems of (a), (b), (c) and (d), unstable O-in-W emulsion is selectively produced by usual up-and-down shaking. It is noted further that the tendency of producing W-in-O emulsion increases with its stability, but the increase of the tendency of producing O-in-W emulsion is not parallel to its stability.

In the heterogeneous system of EEW, there exists foam-nonfoam system, that is, the system which behaves both foamy and non foamy according to the different modes of shaking. It was indicated in the preceding paper(4) that the existence of the foam-nonfoam system is restricted in such a portion of foamy region in the heterogeneous system as it makes, at the same time, a portion of phase inversion zones. In Fig. 4, A′ surrounded by dotted line shows the foamy region of heterogeneous system of EEW, and C represents the zone of phase inversion. Hatched portion, therefore, indicates the foam-nonfoam region. The situation and nature of phase inversion system of EEW is just similar to that of AEW.(4) It foams when it is shaken by the mode (2), while it does not foam by the shaking of the mode (1).

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima for his valuable advice and the inspection of this paper. The expense for the experiment is 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) The mutual solubility curve, tie-lines and the foam stability of homogeneous and heterogeneous system of ethyl alcohol–ethyl ether–water (EEW) were measured. The diagram was established to show the relation between the foam stability and the composition. It shows two maxima of foam stability, one of which is situated along the mutual solubility curve, and the other is on the line of ethyl alcohol–water. The former is more remarkable in its magnitude than the latter as in the system of acetic acid–ethyl ether–water (AEW). The diagram shows the third maximum of foam stability but it is uncertain.

(2) Heterogeneous system of EEW is divided into three portions referring to the type of emulsion produced by shaking, namely, W-in-O region, O-in-W region and phase inversion zone. In W-in-O or O-in-W region, a system simply produces W-in-O or O-in-W emulsion respectively, whatever the modes of shaking, while in the phase inversion zone, a system occasionally produces both types of emulsion according to the two different modes of shaking. In the phase inversion zone, the tendency to produce W-in-O emulsion gradually decreases and the tendency to produce O-in-W emulsion increases as a system changes in composition from those near W-in-O region to those near O-in-W region.

(3) Foam-nonfoam system can also be observed in this system as in AEW or acetic acid–benzene–water system. The region of its existence was determined.

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