Studies on Foams. II.

The Foam Formation and the Volume Contraction of Liquid Mixtures.

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It has been reported, in the preceding paper,(1) that there are the maxima of the foam formation in three regions in the ternary system, ethyl alcohol-glycerol-water, that is the region of small concentration of ethyl alcohol, where the surface tension of the system decreases steeply, the region of large concentration of glycerol, where the viscosity of the system becomes very large, and the region of about 45 per cent of ethyl alcohol. The third maximum is thought to be closely connected with the volume contraction on admixture of the constituent liquids. This may be confirmed by the experiments, on the mixture of methyl alcohol, ethyl alcohol and water which is described in the following lines.

The experimental method is similar to that described in the preceding report. Foaminess and foam duration have been tested by shaking the liquid for 30 seconds in a test tube, measuring the height of foam zone immediately after the end of shaking (A_0 cm.), and the time required to the collapse of foam zone (t sec.). Viscosity η was measured with Ostwald's viscosimeter, and surface tension γ was measured with Traube's stalagmometer. Molar volume contraction ΔV on admixture of liquids (cc./mol.) was calculated from the density data obtained with an Ostwald's pycnometer.

The results obtained are shown in Fig. 1 and Fig. 2. The composition dependence of foaminess A_0 (Fig. 1), and foam duration t (Fig. 2), are entirely parallel with each other, having three maxima, A_1, A_2, and B_1. The maximum B_1 is, perhaps. related with the steep decrease of the surface tension, shown in Fig. 3. The maxima A_1 and A_2, on the other hand, have no relation either to surface tension or to viscosity (Fig 4). These

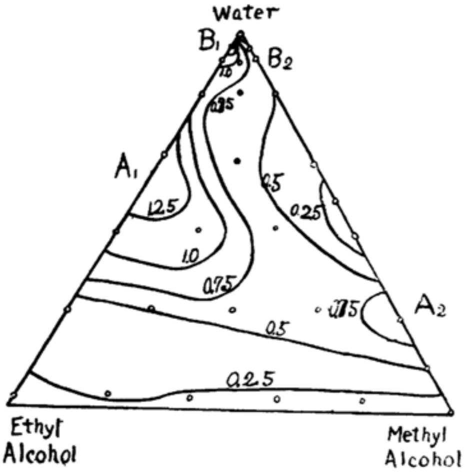

Fig. 1. Foaminess.
A_0 (cm.).

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(1) The first paper, this Bulletin, **21** (1948), 30.

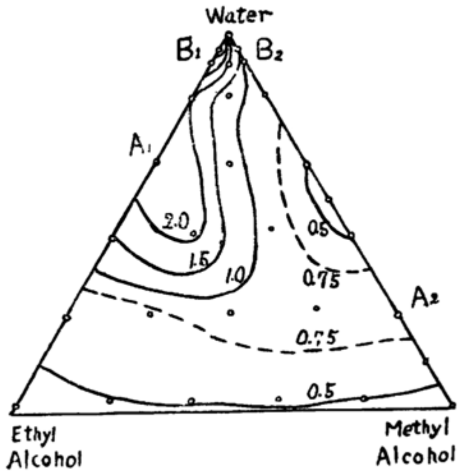

Fig. 2. Foam Duration. t (sec.).

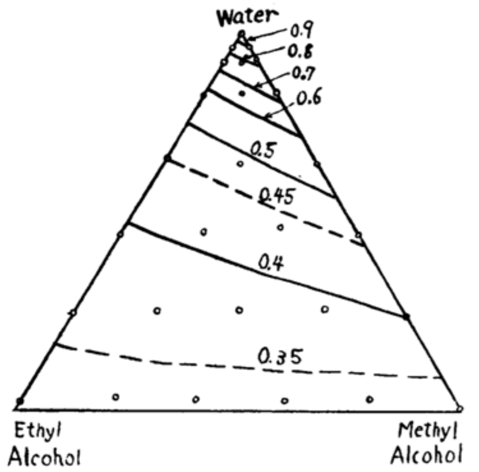

Fig. 3. Surface Tension. γ/γ_w.

maxima seem to have some relation with the volume contraction (Fig. 5). Besides the ternary system, ethyl alcohol-methyl alcohol-water, the following five binary systems have been studied : n-propyl alcohol-ethyl ether, methyl alcohol-ethyl ether, ethyl acetate-ethyl ether, n-propyl alcohol-methyl alcohol and n-propyl alcohol-ethyl acetate. In most of these systems it was confirmed that the molar volume contraction is closely related to the foam formation. The system n-propyl alcohol-ethyl ether and methyl alcohol-ethyl ether have relatively large volume contraction and foam formation. The other systems have small volume contraction or dilatation and little tendency of foam formation.

The binary mixture of the liquid A and B may, generally, be classified into the following three types:

(a). If the molecular interaction between molecules A-B is nearly equal to the average of A-A and B-B, heat of mixing and volume contraction on admixture are both small, and they forms the ideal solution. The systems n-propyl alcohol-methyl alcohol, and methyl alcohol-ethyl alcohol belong to this type, and they do not foam.

(b). If the interaction A-B is smaller than the average of A-A and B-B, heat absorption and volume dilatation may be observed. The system n-propyl alcohol-ethyl acetate belongs to this, and this system does not foam.

(c). If the interaction A-B is larger than the average of A-A and B-B, heat evolution and volume contraction on admixture are observed. In this case, according to McLeod,(2) viscosity-composition curve has a maximum point. Examples are the systems, ethyl alcohol-water and methyl

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(2) McLeod, *Trans. Faraday Soc.*, **19** (1923), 17.

alcohol-water, the foam formation of which becomes maximum at the composition of about 1 : 1.

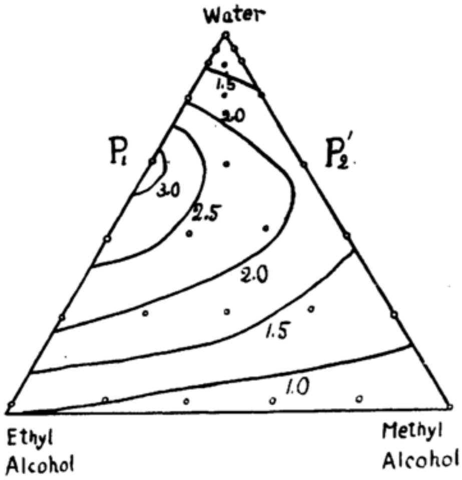

Fig. 4. Viscosity.
η/η_w.

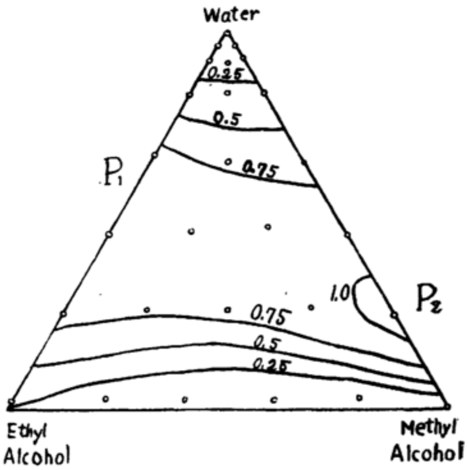

Fig. 5. Volume Contraction.
ΔV (c.c./mol.).

Two mechanisms are proposed on the volume contraction. One is the increase of the average molecular interaction and the decrease of the average molecular distance, which may be corresponding to the case (c) described above. The other is the micelle formation of one of the constituent liquids. By the micelle formation the molecular motion will be restricted in some extent and the free volume of molecules may decrease. The idea that such a micelle is formed not only in aqueous solutions but also in the mixtures of organic liquids was already proposed by S. R. Palit and J. W. McBain.(3) The properties based on the simultaneous presence of the polar and nonpolar portions, or "amphipathic properties", of the solute molecule was considered by G. S. Hartley(4) as an essential factor of micelle formation.

Now a series of solvents, water, acetone, ethyl acetate, and ether will be considered. The hydrophile properties of them become weeker and the organic characters become stronger in this order. They mix with alcohol at any proportion, and according to H. Hirobe,(5) the volume change on admixture is large contraction for water, small contraction for acetone, dilatation for ethyl acetate, and, again, contraction for ether. Micelle may, probably, be formed in water, acetone and ether, but not in ethyl acetate. Therefore, it is supposed that water and acetone have

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(3) S. R. Palit and J. W. McBain, *Ind. Eng. Chem.*, **38** (1946), 741.

(4) G. S. Hartley, "Aqueous Solutions of Paraffin-Chain Salts", London (1936), Chap. 7.

(5) H. Hirobe, *J. Faculty of Sci. Imp. Univ. Tokyo*, Sec. 1, **1**, Part 4 (1926), 155.

a stronger affinity for hydroxyl group of alcohol than for alkyl group, but ethyl acetate has nearly equal affinity for both groups, and ether has a stronger affinity for alkyl group than for hydroxyl group. Then, according to the experiments described above, the liquid mixtures, in which micelle are formed, have foam forming properties.

The foam formation is one of the characteristic properties of the solution. The pure liquid does not foam, however small the surface tension is. This fact was assured by C. W. Foulk and J. N. Miller,(6) T. Nakagawa and J. Sameshima,(7) and others. It is, therefore, supposed that the existence of the Gibbs' adsorption layer at the surface is important for the foam formation. As stated by C. R. Caryl,(8) E. G. King,(9) and G. D. Miles and J. Ross,(10) the surface activity and some other surface chemical properties are closely related to "diphile nature",(11) or "amphipathic nature", of solute molecule, and this is also the cause of micelle formation. It is, therefore, reasonable that the foam formation and micelle formation accompany with each other.

Summary.

The foam formations were tested on the ternary system, methyl alcohol-ethyl alcohol-water, and five binary mixtures. It was found that the volume contraction is closely connected with the foaming properties. This was interpreted in relation to the micelle formation of mixtures.

The author wishes to express his hearty thanks to Professor J. Sameshima for his kind guidance and encouragement.

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(6) C. W. Foulk, *Ind. Eng. Chem.*, **21** (1929), 815; **33** (1941), 1086; C. W. Foulk and J. N. Miller, *ibid.*, **23** (1931), 1283.

(7) T. Nakagawa and J. Sameshima, *J. Chem. Soc. Japan*, **64** (1943), 360.

(8) C. R. Caryl, *Ind. Eng. Chem.*, **33** (1941), 731.

(9) E. G. King, *J. Phys. Chem.*, **48** (1944), 141.

(10) G. D. Miles and J. Ross, *J. Phys. Chem.*, **48** (1944), 280.

(11) Wo. Ostwald, *Kolloid-Z.*, **58** (1932), 179; **60** (1932), 324.