Studies on Foams. VI. Theory of Foam Formation

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It is supposed, in the first instance, that the surface tension may play an important rôle in the foam formation, as it is a surface chemical phenomenon. Plateau's rule(1) states that the liquid of smaller surface tension foams better. This rule is, however, inconsistent with experiences. For instance, pure liquids do not foam at all, both liquid of small surface tension as ethyl ether and liquid of large surface tension as water. This was ascertained by Foulk and Miller(2) and Nakagawa and Sameshima(3). Solutions of surface active substances, such as alcohol or soap, as well as solutions of surface inactive substances as inorganic electrolytes produce foams. As to the aqueous solutions of surface active substances, the surface tension decreases monotonously with the increase of concentration, while the foam formation shows a maximum and again decreases with the further increase of concentration. Considering these facts in all respects, the surface tension seems to have no simple relation to the foam formation. This was already stated by Wo. Ostwald.(4) It is not yet clear what the predominant factor is, though some qualitative ideas have been proposed.

Bartsch(5) proposed "heterogeneity" theory. Talmud and Suchowolskaja(6) suggested a

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(1) *Cf.*, S. Berkmann and G. Egloff: "Emulsions and Foams," New York, (1941), pp. 121.

(2) C. W. Foulk, *Ind. Eng. Chem.*, **21**, 815 (1926); **33**, 1086 (1941); C. W. Foulk and J. N. Miller, *ibid.*, **23**, 1283 (1931).

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

(4) Wo. Ostwald and A. Steiner, *Kolloid-Z.*, **36**, 342 (1925).

(5) O. Bartsch, *Kolloid-Z.*, **38**, 177 (1926).

(6) D. Talmud, S. Suchowolskaja and N. Lubman, *Z. physik. Chem.*, **A151**, 401 (1930); D. Talmud and S. Suchowolskaja, *ibid.*, **A154**, 277 (1931).

relation between foam duration and surface rigidity. Hazlehurst and Neville⁽⁷⁾ stated cybotaxis theory. Sasaki⁽⁸⁾ emphasized that the concentration gradient of surface tension is large when the foam formation is large. Foulk⁽²⁾ proposed balanced-layer theory. These theories are all qualitative. In this report, some semi-quantitative consideration will be given.

When the viscosity of the solution is not too large, the foaminess and foam duration are parallel to each other, while the foaminess is small and foam duration is large, when the solution, such as sulfuric acid or glycerol solutions, is of high viscosity. This has been reported, in the foregoing paper.⁽⁹⁾ Viscous solutions take a long time to flow down the wall of foam, and this is the cause of large duration of foam. Ross⁽¹⁰⁾ and Miles, Leo Shedlovsky and Ross⁽¹¹⁾ carried out some calculations from this point of view. In ordinary solutions, however, the viscosity is not large compared to water, so the effect of it is not large. The effect of viscosity is, therefore, neglected in the following discussion.

The existence of adsorption layer, whether positive or negative, seems to be necessary for the foam formation, since pure liquids do not foam while solutions foam considerably well. This is suggested also by the fact that the dye solution of larger surface activity foams better.⁽¹²⁾ It may be supposed that the collapse of foam occurs when an area, S, of adsorption layer is first removed by some accidental reason, and a crack is formed in this area. If the area of bare surface was smaller than S, the surface might be easily covered again by the thermal motion of adsorbed molecules and foam would not collapse. Let the energy, required to remove the unit area of adsorption layer, be U_Γ. Then, SU_Γ will play just like the activation energy. If the area S does not largely vary by the properties of solution, the foam duration will be parallel to U_Γ.

Let the energy required to remove one mole of solute from adsorption layer to bulk solution be U_1, and the concentration of solute in the solution and the layer be C and C_Γ (mole/cc.), respectively. Then, according to Boltzmann's distribution law:

$$\left.\begin{aligned} C_\Gamma &= C \exp.(U_1/RT) \\ \text{or} \quad U_1 &= RT \ln (C_\Gamma / C). \end{aligned}\right\} \qquad (1)$$

For the positive adsorption, $C_\Gamma > C$ and $U_1 > 0$, and for negative adsorption, $C_\Gamma < C$ and $U_1 < 0$. Let the activity of solute in the solution be a_2, and the molar volume of the solution be V (cc./mole). Then, it is better to replace C by

$$a_2/V. \qquad (2)$$

So equation (1) is written as:

$$U_1 = RT \ln (C_\Gamma V/a_2). \qquad (3)$$

The adsorption layer of the solution of surface active substance may be assumed to be a monomolecular of layer solute molecules lying upon the surface of solution, and the surface film of solute contains no solvent. So the amount of solute contained in the unit area of adsorption layer equals to the surface excess of solute for the unit area of surface, $\Gamma_2^{(1)}$ (mole/cm.²) given by Gibbs' equation:

$$\Gamma_2^{(1)} = -\frac{1}{RT}\frac{\partial \sigma}{\partial \ln (f_2N_2)}, \qquad (4)$$

where σ is the surface tension, f_2 the activity coefficient of solute referred to the infinite dilution as unity, and N_2 the mole fraction of solute. The activity of solute is,

$$a_2 = f_2N_2. \qquad (5)$$

According to the surface chemical studies of higher alcohols, the sectional area of alcohol molecules is said to be about 20 Å². The amount of alcohol molecules closely packed on 1 cm.² of surface, N_a, is, therefore,

$$N_a = 8.33 \times 10^{-10} \text{ (mole/cm.}^2\text{)}. \qquad (6)$$

If the mole volume of pure alcohol is V_2 (cc./mole), the volume of adsorption layer per unit area is N_aV_2. Therefore:

$$C_\Gamma = \Gamma_2^{(1)}/N_aV_2. \qquad (7)$$

So: $$U_1 = RT \ln (\Gamma_2^{(1)} V/f_2N_2N_aV_2). \qquad (8)$$

For electrolytes, the surface excess of solute given by Gibbs' equation $\Gamma_2^{(1)}$ is

$$\Gamma_2^{(1)} = -\frac{1}{\nu RT}\frac{\partial \sigma}{\partial \ln (m\gamma)}, \qquad (9)$$

where m is molality, that is moles of salt per 1000 g. of water, and γ is the mean activity coefficient of salt. The activity of salt a_2 is

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(7) T. H. Hazlehurst and H. A. Neville, *J. Phys. Chem.*, **44**, 592 (1940); *Ind. Eng. Chem.*, **33**, 1084 (1941).

(8) T. Sasaki, *Bull. Chem. Soc. Japan*, **13**, 517 (1938).

(9) M. Nakagaki, *Bull. Chem. Soc. Japan*, **21**, 30 (1948).

(10) S. Ross, *J. Phys. Chem.*, **47**, 266 (1943).

(11) G. D. Miles, Leo Shedlovsky and J. Ross, *J. Phys. Chem.*, **49**, 93 (1945).

(12) M. Nakagaki, This Bulletin, **22**, 200 (1949).

$$a_2 = a_\pm^\nu = (\gamma\, m)^\nu \ (\nu_+^{\nu+}\ \nu_-^{\nu-}) \tag{10}$$

where $\nu = \nu_+ + \nu_-\,.$ (11)

ν is the number of ions formed by the dissociation of one molecule of electrolyte, and ν_+ and ν_- are the numbers of positive and negative ions formed from one molecule respectively. The surface excess given by Gibbs' equation (9) is defined as the amount by which the quantity of solute in the system A, having unit area of surface, exceeds that in the system B, having no surface, when these systems A and B contain the same amount of solvent. This is discussed in detail by Guggenheim and Adam.(13) In this case, the adsorption layer is considered, on the contrary to the case of surface active substances, to contain both solute and solvent. Let the molality of solute in the adsorption layer be m_Γ, and the thickness of adsorption layer be d (Å.). The amount of water contained in 1 cm.^{2} of adsorption layer, that is $d\times 10^{-8}$ cc. is assumed to be $d\times 10^{-8}$ g. Accordingly, by the definition of adsorption amount,

$$\Gamma_2^{(1)} = (m_\Gamma - m)\, d \times 10^{-8}/1000$$

or

$$m_\Gamma = m + \frac{10}{d} \times \Gamma_2^{(1)} \times 10^{10}. \tag{12}$$

Let the mole volume of adsorption layer be V_Γ, the activity of solute in adsorption layer a_Γ, and activity coefficient in adsorption layer γ_Γ. Then,

$$a_\Gamma = (\gamma_\Gamma m_\Gamma)^\nu (\nu_+^{\nu+}\nu_-^{\nu-})$$

and it is better to replace C_Γ by the following terms:

$$a_\Gamma / V_\Gamma = (\gamma_\Gamma\ m_\Gamma)^\nu\ (\nu_+^{\nu+}\ \nu_-^{\nu-})/\nu_\Gamma. \tag{13}$$

From equations (10) and (3), we get

$$U_1 = \nu\ RT \ln \frac{\gamma_\Gamma m_\Gamma V}{\gamma m V_\Gamma}\,.$$

Now, if we assume,

$$V \simeq V_\Gamma \qquad \text{and} \qquad \gamma_\Gamma \simeq 1. \tag{14}$$

then,

$$U_1 = \nu RT \ln \frac{m_\Gamma}{m\gamma}\,. \tag{15}$$

As to the structure of adsorption layer on the aqueous solution of electrolyte, the idea was proposed that the adsorption layer is constructed from pure water by the positive adsorption. The thickness of adsorption layer is calculated under this premise by Rehbinder,(14) Goard,(12) Harkins and McLaughlin,(16) Harkins and Gilbert(17) and some others. The unreasonableness of this idea has already been pointed out by Adam(18). In the present paper the concentration of the adsorption layer is assumed to be m_Γ.

The energy U_1, calculated from equations (8) or (15), is the increase of energy accompanied with the transference of one mole of solute from the adsorption layer to the bulk solution. The energy required to remove the unit area of adsorption layer U_Γ is,

$$U_\Gamma = \Gamma_2^{(1)} U_1\,, \tag{16}$$

where $\Gamma_2{}^{(1)}$ is given by equations (4) or (9). U_Γ is thought to relate to the foam formation of the solution. The change of the free energy of the system, that is the difference of dynamic and static surface tension, is not equal to U_Γ, because the change of free energy accompanying to the change of concentration, from the concentration in the adsorption layer to that in bulk solution, has not been taken into consideration. This change of available energy was not taken out of the system in irreversible process. So the work required to remove the unit area of adsorption layer equals to U_Γ. In the case of electrolytes, both $\Gamma_2^{(1)}$ and U_1 are negative. This means that the concentration is smaller and the energy of solute molecule is higher in the adsorption layer than in the bulk solution, and U_Γ given by equation (16) equals to the energy required to bring solute from interior to surface as far as the concentration of adsorption layer equals to that of the bulk solution.

One of the best investigated system is the aqueous solution of ethyl alcohol. The amount of adsorption in this system has been calculated by Butler and Wightman(19) and Guggenheim and Adam.(13) The adsorption amount is calculated also by the present author using the data of surface tension sited in the "International Critical Tables" and that of activity in the "Landolt-Börnstein's Physikalisch-Chemische Tabellen," using equa-

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(13) E. A. Guggenheim and N. K. Adam, *Proc. Roy. Soc. London*, **A 139**, 218 (1933).

(14) P. Rehbinder, *Z. physik. Chem.*, **111**, 447 (1924); **121**, 103 (1926).

(15) A. K. Goard, *J. Chem. Soc.*, **127**, 2451 (1925).

(16) W. D. Harkins and H. M. McLaughlin. *J. Am. Chem. Soc.*, **47**, 2083 (1925).

(17) W. D. Harkins and E. C. Gilbert, *J. Am. Chem. Soc.*, **48**, 604 (1926).

(18) N. K. Adam, "The Physics and Chemistry of Surfaces," 2nd ed., (1938), Oxford, pp. 125.

(19) J. A. V. Bulter and A. Wightman, *J. Chem. Soc.*, **1932**, 2089.

tion (4). The results agree well with those obtained by the above authors. U_F calculated from equations (4), (8) and (16) is depicted in Fig. 1. Mole volume used in this calculation is obtained from the data of density sited in the "International Critical Tables." The same calculation has been done for methyl alcohol and the results are shown in Fig. 1.

The method of the observation on foam formation is the same as that described in the preceding paper.(20) Twenty cc. of solution is shaken in a test tube of 40 cc. in capacity. The maximum height of foam zone after shaking A_m (cm.) and the time required to collapse the foam zone t_0 (sec.) are recorded and plotted in Fig. 1. Experiments were done at room temperature of about 25°. As already reported in the foregoing reports(9),(21), two maxima of foam formation are observed at the concentration of about 3 % and 30 % for ethyl alcohol, and about 5 % and 50 % for methyl alcohol. The general tendency of curves agrees well with that of U_F. Relation between curves for methyl and ethyl alcohol is also similar to that of U_F.

As U_1 is the energy required to transfer one mole of solute from absorption layer to the bulk solution, U_1 is supposed to be a function of concentration of solution. In dilute solution, the energy required to bring the hydrophobic alkyl group of alcohol molecule into the solution, shoving water molecules aside, will be large. In concentrated solution, however, the value of U_1 will be small, since alcohol dissolves many organic substances well. In fact, U_1 calculated by equation (8) becomes smaller as the concentration increases.

Though electrolytes are surface inactive, their solutions foam considerably well as studied by Talmud and Suchowolskaja(22) and others. The foaminess A_m and foam duration t_0 measured by the method described above by the present author, and U_F calculated from equations (9), (12), (15) and (16) are depicted in Fig. 2. Data used in this calculation are taken from the "International Critical Tables" for surface tension, and from the report by Robinson and Harned(23) for the activity coefficient. The thickness of the adsorption layer d (Å.) in equation (12) is taken so as the tendency of calculated curve agree with that of the observed. The values of d are cited in Table 1. It is about 4 Å. for chlorides and nitrates, about 7 Å. for sulfate, and about 9

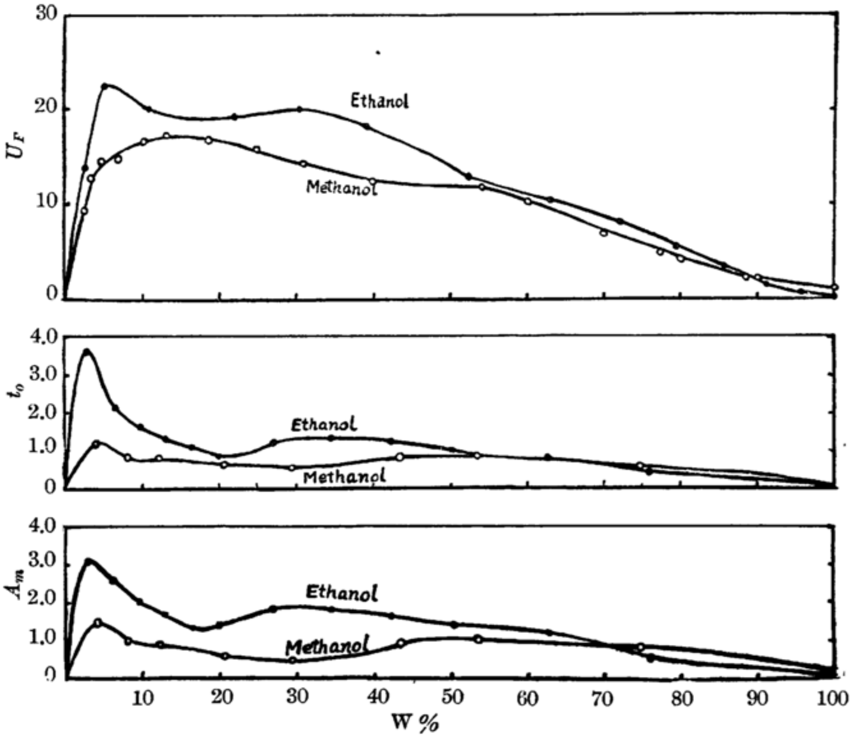

Fig. 1.—Alcohol solutions.

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(20) M. Nakagaki, This Bulletin, **23**, 102 (1950).
(21) M. Nakagaki, This Bulletin, **22**, 21 (1949).
(22) D. Talmud and S. Suchowolskaja, *Z. physik. Chem.*, **A154**, 277 (1931).
(23) R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

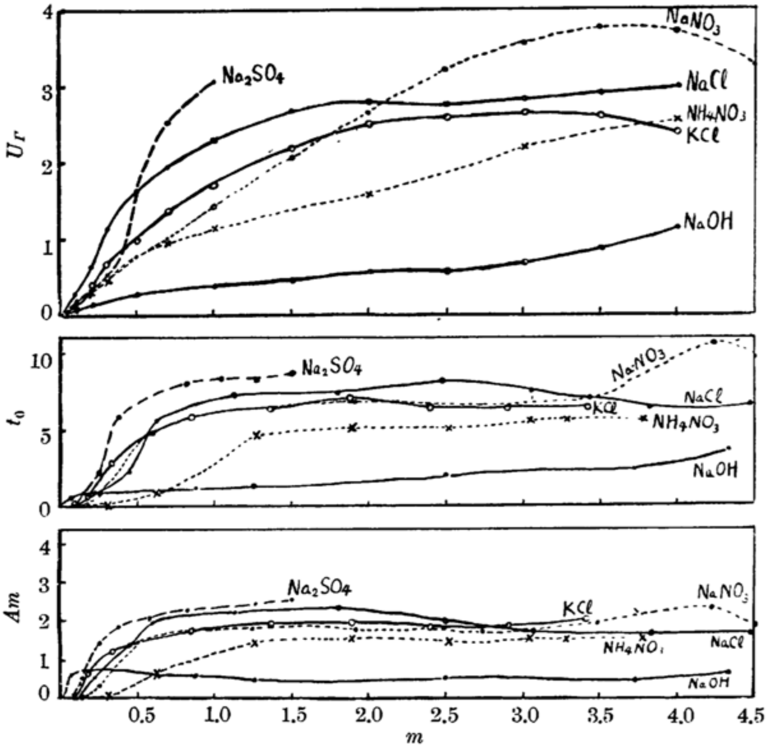

Fig. 2.—Electrolyte solutions.

Table 1

Value of d, Å.

NaCl	4.0	$NaNO_3$	3.6	Na_2SO_4	6.8
KCl	3.8	NH_4NO_3	4.4	NaOH	9.0

Å. for hydroxide. Factors determining the thickness of adsorption layer is not yet clear, but following qualitative consideration may be acceptable. Since ions are hydrated in aqueous solution, the distance from the surface to ions lying nearest to the surface is greater than the radius of hydrated ion, if ion is surrounded by the same thickness of the layer of bound water as in the interior of solution, even when the ion is entered in the adsorption layer. This may be one of the reasons of the negative adsorption of ions. It is usual, moreover, that the negative ion approaches to the surface closer than the positive one. This has been assured by many experiments on the surface potential. The thickness of the adsorption layer will, therefore, relate to the degree of the hydration of anion. This idea is supposed by the fact that the sequence of the thickness of adsorption layer,

$$NO_3^-,\ Cl^- < SO_4^{--} < OH^-$$

agrees with the lyotropic series. In addition, the thickness of adsorption layer agrees with the radius of hydrated anions in its order of magnitude.

Summary

Foam formation of aqueous solutions of both alcohols and electrolytes are accounted under the assumption of parallelism between the foam formation and the energy required to remove the unit area of adsorption layer from the surface. The maximum observed at the concentration of about 45 % for alcohol solutions are also accounted. The relative relation between some electrolyte solutions is accounted under the assumption that the thickness of adsorption layer increases in the sequence of lyotropic series of anions: Cl^-, $NO_3^- < SO_4^{--} < OH^-$.

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