Studies on Foams. VII. Theory of Foam Formation of Dyestuff Solution

By Masayuki NAKAGAKI

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In the preceding paper⁽¹⁾ the close relation between the foam formation and the work required to remove the unit area of adsorption layer, U_Γ, has been found for alcohol solutions and electrolyte solutions. The theory will be extended, in the present paper, to dyestuff solutions. The calculation of the work U_Γ was based, in the preceding paper, upon the observed data of the surface tension, but it is, now, replaced by a molecular kinetic theory.

Let the energy required to remove one mole of solute from the adsorption layer to the bulk solution be U_0, and the concentration of solute in the solution and in the layer be C and C_Γ (mole/cc.), respectively. U_0 is such as an adsorption potential. The velocity of desorption, G_d (mole/cm.²/sec.), that is the moles of molecule passing through the unit area in the unit time from the adsorption layer to the bulk solution is calculated as follows. If the velocity distribution of solute molecules in the adsorption layer obeys to Maxwell-Boltzmann's distribution law, the velocity component in x direction, that is the direction normal to the surface, is in the average,

$$\overline{v_x(0)} = 2\sqrt{\frac{kT}{2\pi m}} \qquad (1)$$

If a molecule goes and returns between the upper and lower boundaries of adsorption layer, of thickness d (cm.), with the velocity $\overline{v_x(0)}$, the frequency $\bar{\nu}_0$ is, since the path in one period is $2d$,

$$\bar{\nu}_0 = \frac{\overline{v_x(0)}}{2d} = \frac{1}{d}\sqrt{\frac{kT}{2\pi m}} \qquad (2)$$

This is analogous to the well known equation in the statistical mechanics of liquid. As for liquid, two models are often used as the first approximations: "smooth potential model" and "harmonic oscillator model". Free volume

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(1) M. Nakagaki, This Bulletin, **23**, 127 (1950).

per molecule v in the smoothed potential model and the frequency of molecule ν in harmonic oscillator model are related with each other by the equation⁽²⁾:—

$$\nu=\frac{1}{v^{1/3}}\sqrt{\frac{kT}{2\pi m}}\,. \tag{3}$$

Eq. (2) is the one dimensional analogue of Eq. (3). From this point of view, it will be permitted to apply the kinetic theory of gas to the adsorption layer.

The average x-component velocity of molecules, having the kinetic energy greater than U_0/N_0, is,

$$\bar{v}_x(U_0)=\frac{kT}{A(U_0)}\exp\left(-U_0/RT\right) \tag{4}$$

where

$$A(U_0)=\int_{\sqrt{(2/m)(U_0/N_0)}}^{\infty}\exp(-mv_x^2/2kT)\mathrm{d}v_x \tag{5}$$

and N_0 is Avogadro's number. Therefore, from Eq. (2),

$$\bar{\nu}=\frac{\bar{v}_x(U_0)}{2d}=\frac{kT}{2dA(U_0)}\exp\left(-\frac{U_0}{RT}\right) \tag{6}$$

Let the moles of solute contained in the unit area of the adsorption layer be n_0, and the moles of solute molecule having the kinetic energy greater than U_0 be n, then

$$n/n_0=2A(U_0)/\sqrt{2\pi mkT} \tag{7}$$

and

$$n_0=d\cdot C_\Gamma \tag{8}$$

Therefore:

$$n=2dA(U_0)C_\Gamma/\sqrt{2\pi mkT} \tag{9}$$

If all the molecules, colliding to the boundary between the adsorption layer and the bulk solution with the kinetic energy greater than U_0, desorb, then the rate of desorption G_d is,

$$G_d=n\bar{\nu}=C_\Gamma\sqrt{kT/2\pi m}\exp\left(-U_0/RT\right) \tag{10}$$

Then, calculate the adsorption velocity. Let the saturation amount of adsorption per unit area be N_a (mole/cm.²), the actually adsorbed amount be $\Gamma_2^{(1)}$, and the area already occupied be $\Gamma_2^{(1)}/N_a$. Among the molecules colliding to the surface already occupied, α is assumed to be adsorbed and $(1-\alpha)$ be repelled, and all molecules colliding to the the empty surface $(1-\Gamma_2^{(1)}/N_a)$ is assumed to be adsorbed. The total number of molecules colliding to the surface is $(C/2)\overline{v_x(0)}=C\sqrt{kT/2\pi m}$, so the rate of adsorption G_a, that is the moles of solute adsorbed in unit time per unit area, is

$$G_a=\left\{\left(1-\frac{\Gamma_2^{(1)}}{N_a}\right)+\alpha\frac{\Gamma_2^{(1)}}{N_a}\right\}\cdot C\sqrt{\frac{kT}{2\pi m}} \tag{11}$$

In dynamic equilibrium,

$$G_d=G_a \tag{12}$$

The volume of the adsorption layer per unit area is N_aV_2, where V_2 is the mole volume of solute. Then,

$$C_\Gamma=\Gamma_2^{(1)}/N_aV_2 \tag{13}$$

Therefore,

$$\Gamma_2^{(1)}=\frac{N_akC}{1+(1-\alpha)kC} \tag{14}$$

where

$$k=V_2\exp\left(U_0/RT\right) \tag{15}$$

or

$$\frac{C_\Gamma}{C}=\frac{1}{1+(1-\alpha)kC}\exp\left(\frac{U_0}{RT}\right) \tag{16}$$

When the adsorbed molecules occupy definit sites on the adsorption surface, the molecules colliding to the area already occupied are all repelled, that is $\alpha=0$. Then Eq. (14) becomes:—

$$\text{when}\quad \alpha=0,\quad \Gamma_2^{(1)}=\frac{N_akC}{1+kC} \tag{17}$$

This agrees with Langmuir's equation. When the adsorbed molecule moves freely on the surface and the collision diameter of the molecule is not great, all the molecules colliding to the adsorption surface are thought to be adsorbed. In this case, $\alpha=1$, Eq. (16) becomes:

$$\text{when}\quad \alpha=1,\quad C_\Gamma/C=\exp\left(U_0/RT\right) \tag{18}$$

which is in agreement with Boltzmann's equation used in the preceding paper,⁽¹⁾ for alcohol solutions.

Eq. (16) is rewritten as:

$$\left.\begin{aligned} &C_\Gamma/C=\exp\left(U_1/RT\right)\\ \text{where}\quad &U_1=U_0-RT\ln\{1+(1-\alpha)kC\}\end{aligned}\right\} \tag{19}$$

U_1 is the energy required to remove one mole of solute from the adsorption layer to the bulk solution. $R\ln\{1+(1-\alpha)kC\}$ is the entropy corresponding to the assumption that, $(1-\alpha)$ of molecules colliding to the surface are repelled. This gives the impression as if the transposition of molecule from the adsorption layer to the bulk solution is easier in the case when the repelling is present. In the case of triphenylmethane dyes, the molecules are considered as plates of about 4 Å. in thickness and 200 Å.² in area, and the adsorbed molecules

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(2) R. H. Fowler and E. A. Guggenheim: "Statistical Thermodynamics", Cambridge, 1939, p. 324.

are lying parallel to the liquid surface. Almost all molecules colliding to the "already occupied area" are, therefore, repelled, and α is assumed nearly equal to zero. Eq. (19) then becomes,

$$U_1 = U_0 - RT \ln (1+kC). \qquad (20)$$

Gibbs' equation is, if the activity coefficient of solute is assumed to be equal to unity for the dilute solution,

$$\Gamma_2^{(1)} = -(1/RT)(\partial\sigma/\partial \ln C) \qquad (21)$$

Using this and Langmuir's equation (17), and assuming that k or U_0 is independent to concentration,

$$1-\sigma/\sigma_0 = (N_a RT/\sigma_0) \ln (1+kC) \qquad (22)$$

is obtained. Rewriting the natural logarithms to the common one,

$$1-\sigma/\sigma_0 = A \log (1+kC) \qquad (23)$$

$$\text{where} \quad \left.\begin{aligned} A &= 2.303 \times N_a RT/\sigma_0 \\ k &= V_2 \exp (U_0/RT) \end{aligned}\right\} \qquad (24)$$

Eq. (24) agrees with the results cited in Freundlich's "Kapillarchemie," Vol. 1, p. 84. Eq. (23) is the well known Szyszkowsky's experimental equation, which is recognized as to fit well with many experimental data.

Table 1

Areas Occupied by Some Radicals

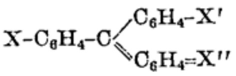
Triphenyl methane nucleus	 $X\text{-}C_6H_4\text{-}C\begin{matrix}\diagup C_6H_4\text{-}X' \\ \diagdown\!\!\diagdown C_6H_4{=}X''\end{matrix}$	116 Å.^{2}
Methyl group	CH_3-	12.5 Å.^{2}
Hydrogen atom	H-	4.5 Å.^{2}
Ethyl group	C_2H_5-	19 Å.^{2}
Benzyl group	C_6H_5-CH_2-	45 Å.^{2}
Thickness of molecule (equal to that of benzene)		37 Å.

Table 2

Dimensions of Dye Ions

Dye	Formula weight M	Area of ion S, 10^{-16} cm.^{2}	Saturated adsorption amount Na, 10^{-10}mole/cm.^{2}	Mole volume V_2, cc./mole	Density d
Methyl violet 5B	448	223.5	0.743	498	0.898
Brilliant green	385	192	0.864	428	0.899
Malachite geeen	329	166	1.000 •	370	0.889
Crystal violet	372	191	0.868	426	0.873

Size of dye molecule is calculated using van der Waals radii cited by Pauling⁽³⁾. The area of benzene molecule is calculated as 38.7 Å.^{2}, if C–C distance is assumed to be 1.39 Å., C–H distance 1.07 Å. and van der Waals radius of hydrogen atom 1.2 Å. The area of benzene molecule is calculated as 39.7 Å.^{2}, by the assumption that the density is 0.88, and the thickness is 3.7 Å. These two values of the area of benzene molecule agree well with one another. The radical $(X\text{-}C_6H_4\text{-})_3C$ may be called as "triphenyl methane nucleus", (where X is hydrogen or nitrogen atom). The triphenyl methane nucleus is generally thought to have a triangular co-planar structure⁽⁴⁾. The area of it is assumed to be equal to about three times as large as that of benzene, 116 Å.^{2} Radii of hydrogen atom and methyl radical are assumed to be 1.2 Å. and 2.0 Å., respectively. Areas of various radicals calculated as above are cited in Table 1. Areas, S, of some dye ions calculated by the summation of data of Table 1 are shown in Table 2. The thickness of ions are assumed to be equal to that of benzene, or 3.7 Å. The saturated adsorption amount per 1 cm.^{2}, N_a (mole/cm.^{2}), is calculated from the value of area, S, by the equation,

$$N_a = 1/(N_0 S) = 1.66 \times 10^{-24}/S \qquad (25)$$

where N_0 is Avogadro's number. Mole volume of dye ion in the adsorption layer, V_2 (cc./mole), is obtained, assuming the thickness of the adsorption layer being equal to the thickness of ion,

$$V_2 = 3.7 \times 10^{-8}/N_a \qquad (26)$$

The density of it, d, is

$$d = M/V_2 \qquad (27)$$

where M is the formula weight of dye ion. These values are also shown in Table 2. The density data cited are $0.8 \sim 0.9$, which are fairly smaller than the value of solid dye, that is about 1.5, and is rather similar to the value of benzene, 0.88. This is quite plausible, since the molecular interaction in the adsorption layer is fairly weaker than in the crystal state.

Using these values, the coefficient A is calculated from Eq. (24). The value of k is determined so as the experimental values fit the Szyszkowsky's equation (23) best. The value of U_0 is then calculated according to Eq. (24). These are cited in Table 3. In Table 3, E is:

$$E = U_0/SN_0 \qquad (28)$$

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(3) L. Pauling, "The Nature of the Chemical Bond," New York, 1940, p. 189.

(4) See, *e. g.*, E. Hückel, *Z. Elektrochem.*, **43**, 827 (1937); G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**. 273 (1939).

Table 3

Constants for Adsorption (20°C.)

Dye	A	k, 10^6cc./mole	U_0, 10^{10}erg/mole	E, erg/cm.^{2}
Methyl violet 5B	0.0573	90.4	29.5	21.9
Brilliant green	0.0667	6.1	23.3	20.1
Malachite green	0.0771	2.40	21.4	21.4
Crystal violet	0.0670	1.71	20.2	17.6

It should be noticed that E is nearly equal to 20 erg/cm.^{2} for all dyes.

Using these data, U_1 and $\Gamma_2^{(1)}$ are obtained from Eqs. (20) and (17), respectively. As the product of them:

$$U_\Gamma = \Gamma_2^{(1)} U_1 \tag{29}$$

the energy required to remove the unit area of the adsorption layer U_Γ is calculated. According to the preceding paper(1), U_Γ should be parallel to the foam formation of the solution. In Fig. 1, calculated values of U_Γ are plotted along with the foaming ability F reported in the third paper of this series.(5) In these triphenyl methane dyes, only methyl violet 5B has a maximum point in its foaming ability-concentration curve. It has been supposed in that paper that this will be due to the enormously large surface activity of this dye. By the calculation in this paper, it is shown that $U_\Gamma - C$ curve has a maximum point for methyl violet 5B, while for other dyes no maximum is obtained. The qualitative discussion done in the former paper has been, therefore, justified in this paper.

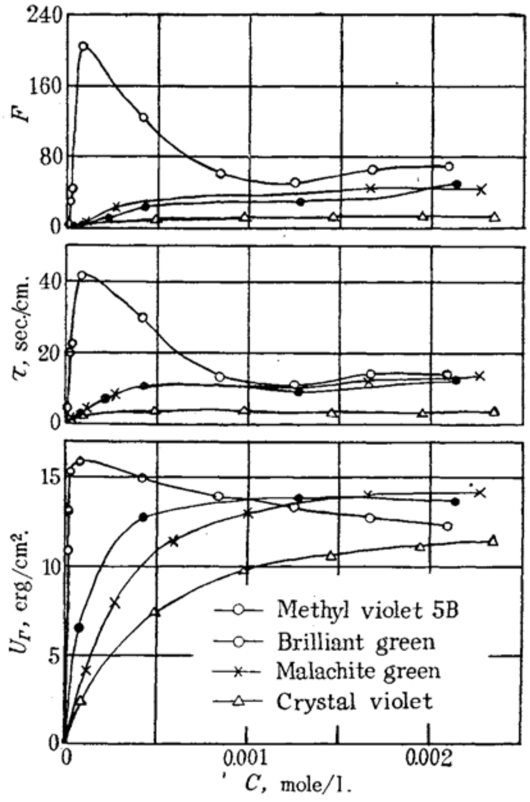

Fig. 1.—The Relation of F and U_Γ to C.

The fact that E is nearly equal to 20 erg/cm.^{2} suggests an interesting property of the adsorption layer. As described before, the property of the adsorption layer of triphenyl methane dye is somewhat similar to benzene. This is suggested both from its molecular structure and from its density cited in Table 2. Therefore,

$$E \doteqdot u_w + u_{w-0} - u_0 \tag{30}$$

where u_w, and u_0 are internal surface energy of water and benzene, respectively, and u_{w-0} is internal interfacial energy of water-benzene interface. According to International critical Tables,(6)

$$\left.\begin{aligned} u_w &= 118.15 \quad \text{erg/cm.}^2 \\ u_0 &= 67.86 \quad \text{erg/cm.}^2 \\ u_{w-0} &= 52.00 \quad \text{erg/cm.}^2 \end{aligned}\right\} \tag{31}$$

at 20°C. From these data,

$$E \doteqdot 102.3 \quad \text{erg/cm.}^2 \tag{32}$$

is obtained, which is fairly different from the experimental value: $E \simeq 20$ erg/cm.^{2} cited in Table 3. This discrepancy may be ascribed to the fact that the layer of "benzene" is a thin layer of 3.7 Å., so that u_0 and u_{w-0} is different from the value for the bulk of benzene.

Fowler(7) calculated the adhesion energy and obtained

$$E_{1-2}^{adh} = 2\pi \int_0^\infty n_2(j)\mathrm{d}j \int_j^\infty \mathrm{d}f \int_f^\infty n_1(f-j)\, \epsilon_{12}(r) r\mathrm{d}r \tag{33}$$

where E_{1-2}^{adh} is the adhesion energy between phase 1 and phase 2 per unit area, $\epsilon_{12}(r)$ is the interaction energy between molecules distant as r from each other, n_1 and n_2 are the densities of molecules (number of molecules/cc.) in both phases, and j, f, and r are the distances shown in Fig. 2.

For simplicity, it is taken as

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

(6) "International Critical Tables", Vol. IV, p. 436.

(7) Fowler, *Proc. Roy. Soc.*, **A 159**, 229 (1937).

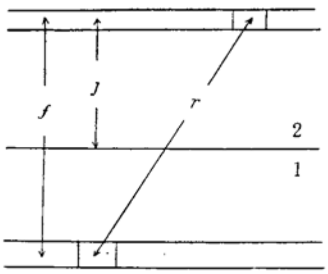


Fig. 2.

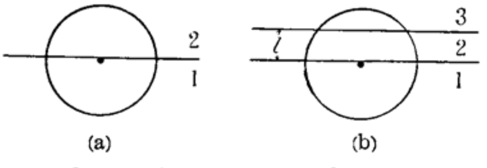
$$n_1(f-j)=N_1,\quad n_2(j)=\begin{Bmatrix}0 & \text{if } j<R_{12}\\ N_2 & \text{if } j\geqq R_{12}\end{Bmatrix}\quad \text{and}\quad \epsilon_{12}=-\mu_{12}/r^6 \qquad (34)$$

where, N_1 and N_2 are constants, showing the density in the bulk of phases 1 and 2, respectively, R_{12} is the sum of radii of molecules 1 and 2, and μ_{12} is a constant. Under these assumption, the equation (33) is simplified as,

$$E_{1-2}^{adh}=-(\pi/12)N_1N_2\mu_{12}/R_{12}^2 \qquad (35)$$

Then, let u_1, u_2 and u_{12} be the internal surface energy of phases 1, 2, and the internal interfacial energy between phases 1 and 2, respectively. It is obtained that,

$$\begin{aligned}u_1&=-E_{1-1}^{adh}/2=(\pi/24)N_1^2\mu_{11}/R_{11}^2\\ u_2&=-E_{2-2}^{adh}/2=(\pi/24)N_2^2\mu_{22}/R_{22}^2 \qquad (36)\\ u_{12}-u_1-u_2&=E_{1-2}^{adh}=-(\pi/12)N_1N_2\mu_{12}/R_{12}^2\end{aligned}$$



(a) (b)

Fig. 3.—A schematic explanation of interfacial energy.

The interfacial energy is sometimes schematicaly explained in a text-book as shown in Fig. 3 a. For a molecule of phase 1, placed at the surface, the lower half of its sphere of action is filled with molecules of phase 1, and the upper half is filled with molecules of 2, if the thickness of both phases are large enough compared with the radius of the action. The difference of the interactions from two hemispheres causes the interfacial energy between 1 and 2. If, then, the thickness of the layer 2 is smaller than the radius of the sphere, as shown in Fig. 3 b, the interfacial energy between phases 1 and 2 will be different from the ordinary value corresponding to Fig. 3 a. Modifying Fowler's equation (33), the adhesion energy between the bulk phase 1 and the layer 2, thickness of which is l, (Fig. 3 b), is expressed as:

$$E_{1-23}^{adh}=2\pi N_1\int_0^l n_2(j)\mathrm{d}j\int_j^\infty \mathrm{d}f\int_f^\infty \epsilon_{12}(r)r\mathrm{d}r +2\pi N_1\int_l^\infty n_3(j)\mathrm{d}j\int_j^\infty \mathrm{d}f\int_f^\infty \epsilon_{13}(r)r\mathrm{d}r \qquad (37)$$

This is integrated, besides with assumption (34), under the following additional assumption that

$$n_3(j)=N_3,\quad (\text{if } j\geqq l) \text{ and } \epsilon_{13}(r)=-\mu_{13}/r^6 \qquad (38)$$

and obtained that

$$E_{1-23}^{adh}=-\frac{\pi N_1}{12}\left\{N_2\,\mu_{12}\left(\frac{1}{R_{12(3)}^2}-\frac{1}{l^2}\right)+N_3\mu_{13}\frac{1}{l^2}\right\} \qquad (39)$$

As the shortest distance between the centers of gravity of molecule 1 and 2 may be different from the value of R_{12} by the orientation of molecule in the thin layer, it is shown as $R_{12(3)}$. Using Eq. (36),

$$E_{1-23}^{adh}=(u_{12}-u_1-u_2)\left(\frac{R_{12}^2}{R_{12(3)}^2}-\frac{R_{12}^2}{l^2}\right)+(u_{13}-u_1-u_3)\,\frac{R_{13}^2}{l^2} \qquad (40)$$

is obtained.

The energy required to bring a dye molecule (per unit area) from the adsorption layer into the bulk solution, E, is expressed

$$E=-E_{w-w}^{adh}+E_{w-ow}^{adh} \qquad (41)$$

In Eqs. (36) and (40), let $1=w$, $2=o$, and $3=w$. Then, under the notice that $u_{ww}=0$, Eq. (41) is rewritten:

$$E=2u_w\left(1-\frac{R_{ww}^2}{l^2}\right)+(u_{wo}-u_w-u_o)\left(\frac{R_{wo}^2}{R_{wo(w)}^2}-\frac{R_{wo}^2}{l^2}\right) \qquad (42)$$

If $R_{wo(w)}=R_{wo}$ and $l\gg R_{wo}$, this equation coincides with Eq. (30).

Molecular diameter of water, R_{ww}, is calculated from the density, ρ_w, molecular weight, M_w, and mole volume, V_w, of water and Avogadro's number, N_0,

$$R_{ww}=\frac{1}{\gamma}\left(\frac{V_w}{N_0}\right)^{1/3}=\frac{1}{\gamma}\left(\frac{M_w}{\rho_w N_0}\right)^{1/3} \qquad (43)$$

γ, a constant determined by the molecular arrangement, is assumed rather arbitrarily,

$$\gamma = 0.935, \tag{44}$$

referring to the facts that $\gamma=1$ for simple cubic lattice, $\gamma=0.916$ for the body centered lattice, and $\gamma=0.890$ for the face centered lattice. Then, R_{ww} is calculated as:

$$R_{ww}=3.32\,\text{Å}. \tag{45}$$

For benzene, a similar calculation gives,

$$R_{oo}=5.64\,\text{Å}. \tag{46}$$

and

$$R_{wo}=\left(\frac{R_{ww}+R_{oo}}{2}\right)=4.48\,\text{Å}. \tag{47}$$

It has already been shown by the assumptions in Eq. (34), the boundary surface between phases 1 and 2 is taken as a plane placed on the centers of the phase 1 molecules nearest to phase 2. Then, using the value of the thickness of benzene molecule, δ, or 3.70 Å.,

$$\left.\begin{aligned} R_{wc(w)}&=\frac{1}{2}R_{ww}+\frac{1}{2}\delta=3.51\,\text{Å}. \\ l&=\frac{1}{2}R_{ww}+\delta=5.36\,\text{Å} \end{aligned}\right\} \tag{48}$$

Then, by Eq. (42),

$$E=21.0\,\text{erg/cm.}^2 \tag{49}$$

is obtained. This agrees well with the values in Table 3, that is $E\simeq 20\,\text{erg/cm.}^2$

Summary

Considering the dynamic equilibrium of adsorption and desorption on the surface of water, Szyszkowsky's equation is derived. Using the area of dye molecule calculated from the molecular structure, U_o and $\Gamma_2^{(1)}$ are estimated to obtain the best conformity with the measurement of the surface tension. U_r calculated by them is compared with the foam formation of these triphenyl methane dyes. Maximum observed in the foaming ability—concentration curve of methyl violet 5 B is explained by its large surface activity. The fact that the energy required to bring the unit area of dye molecule into the bulk solution is about 20 erg/cm.^{2} is justified using the correction of interfacial energy due to the fact that the thickness of the adsorption layer is nearly equal to the dimension of the range of molecular force.

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