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A Survey of the Laws of Foam Formation and Its Applications in Separation Processes

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Abstract

This study summarizes various laws of foam formation, foam rheology, and foam drainage. It also discusses different forces—Laplace capillary suction, van der Waals interaction, electric double layer, and steric factor—acting in drainage of foams. In addition, recent work on phase equilibria and foam stability and the use of foam in fractionation and extraction processes is reviewed. Finally, it presents the possibility of using foam in gas cleaning and a theoretical model for gas cleaning by foam.

INTRODUCTION

Effectively, all the industrial processes—precipitation, crystallization, dispersion, flocculation, wetting and formation and breaking of foams and emulsions—depend on the application of surface phenomena. These systems contain interfaces—liquid/vapor, liquid/liquid, liquid/solid, and solid/vapor—which are responsible for surface phenomena. With the rapid advances in the chemical process industry, considerable interest has developed in studying these interfaces. More recently, however, the emphasis has shifted to the behavior of foams; individual films have been studied, mainly to detect factors affecting the collective behavior of the many films in a foam (*1*). Foams are utilized in the chemical industry to

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provide a large interface for reacting gases. Traditionally, the separation processes are based on extraction, precipitation, distillation, or adsorption. Among these processes is foam separation, which depends on selective adsorption of solutes from the solution. Foam separation has various uses, such as the concentration and recovery of valuable solutes from dilute streams and the treatment of industrial waste. It is also a useful tool in dealing with problems of environmental pollution.

A closely related subject of industrial importance is the breakdown of emulsions and foam in which the last separation of droplets before their coalescence must be effected by a thin film analogous to a surfactant film in air. The successful application of foams in industry depends on a better understanding of the related laws of physics and chemistry, which are responsible for the formation and destruction of thin films and foams. A great deal of research has been developed since 1860 when Plateau first described the laws of foam formation (*2*). It is the purpose of this communication to compile the most relevant information on the properties of foams in order to achieve a better understanding of foam formation and destruction for the purpose of using foams in separation and other processes.

LAWS OF FOAM FORMATION

Foam—a dispersion of a relatively large volume of gas in a relatively small volume of liquid—has been known from the time of Robert Boyle. In 1873 Plateau gave the laws of bubble geometry which constitute the basis of foam structures (*3*):

1. Three, and only three, foam lamellae meet at an edge; the three coplanar angles at which they are inclined to each other are all equal. Hence, each is 120°.
2. Four, and only four, of these edges meet at one point, the angles at which they meet are equal to 109°28′16″ (the tetrahedral angle).

These laws are valid for all assemblies of bubbles in equilibrium based on the minimizing of the surface area of liquid films.

In 1867 Tait presented the geometric calculations for the special case of two bubbles uniting to form a single sphere.

Ross (*3*), using these geometric calculations, has modified the equation for foam:

$$3P\,\Delta V + 2\nu\,\Delta A = 0 \qquad (1)$$

where P is the pressure, ΔV is the diminution of the whole volume occupied by the air, ΔA is the surface of liquid film, and v is the surface tension.

The Tait-Ross Eq. (1) describes the conditions of energy transfer with the decrease of an interfacial area resulting from gas transfer between spherical bubbles submerged in a liquid, whether the mechanism of transfer be the results of the coalescence of bubbles or the diffusion of gas through the liquid medium that separates the bubbles.

The reduction of the interfacial area is, therefore, accompanied by a gain in total free energy and hence, foams, like other irreversible colloids, are unstable in a thermodynamic sense.

The stability of foam depends completely upon the conditions in the lamellae. If the transport in the lamellae is completely Newtonian, the foam is a *transient* type, but if this transport reaches a stage where it decreases considerably when the lamellae is thinning, the foam is *persistent.*

A persistent foam is characterized by the fact that a disturbance of a lamella is cured or resisted by elastic effects. There are two well-known theories of elasticity of surfactant solutions due to Marangoni and Gibbs.

The Marangoni effect arises from the fact that an expanding surface on a dilute solution of a surfactant has a somewhat higher surface tension than the static value for the solution. Any extension of a surface is accompanied by an increase of free energy. The elasticity of foam lamellae is generally attributed to a rise in surface tension, which counteracts further extension of the surface. A certain amount of free energy is needed for the extension of the surface, even if the surface tension remains constant.

For a liquid film of surface area A, which is extended to dA due to local disturbances in the film and a change in surface tension dv, the free energy change is represented by

$$dF = v\,dA + (A + dA)\,dv \tag{2}$$

Gibbs (*4*) determined the value of free energy with surface tension change in a film containing two components.

The elasticity of foam lamellae is generally attributed to a rise in surface tension which counteracts further extension of the surface. Gibbs defined the modulus of surface elasticity as the stress divided by strain per unit area. Because of the two faces of the film, the surface elasticity is given as

$$E = 2A\frac{dv}{dA} \tag{3}$$

The value of surface elasticity, E, may be determined by combining

Eqs. (2) and (3) and by considering conditions $dA \ll A$ in Eq (2) with a change in surface tension. This gives

$$dF = \left(v + A\frac{dv}{dA}\right)dA$$
$$= \left(v + \frac{1}{2}E\right)dA$$

$\frac{1}{2}(E/v)$ gives the Gibbs "surface elasticity."

The value of E may be calculated from the change in surface tension dependent on the activity of surface active solute (*5*).

Kitchener and Cooper (*6*) determined the surface elasticity by measuring the change in surface tension as a function of the lamellae thickness for an anionic surfactant. The relation used was a modification of Eq. (3):

$$E = -2\,dv/d\ln l \tag{4}$$

where l is the thickness of the lamellae.

Kitchener and Cooper (*6*) concluded from their results that there are some weak restoring forces opposing the thinning at a thickness of about 10^{-2} cm in a very dilute solution. Large forces appear in concentrated solutions, but only when the lamellae are very thin.

Mysels et al. (*7*) devised a technique for determining the coefficient of elasticity of mobile and rigid soap films. A foam suspended with a sensitive electrical dynamometer can record the force acting on the frame during corresponding changes in the surface tension. Mysels et al. determined the coefficient of elasticity to be about 15 dynes/cm for a mobile film and about 100 dynes/cm for rigid films.

Liquid lamellae, containing only one component, collapse very rapidly irrespective of the value of surface tension. Persistent and transient foams have a liquid phase which contains at least two components, one of which is preferentially adsorbed at the interface, giving rise to the essential element of elasticity.

In a two-component system, a solute which decreases the surface tension of the solution will concentrate in the surface layers. A solute that increases the surface tension concentrates in the bulk liquid. According to Gibbs, the increase in concentration of a single surface active material at a gas liquid interface can be represented by

$$\Gamma = \frac{-c}{RT}\frac{dv}{dc} \tag{5}$$

where c is the concentration in g mole/cm^3, v is the surface tension in dynes/cm and the surface excess of solute in g mole/cm^2, R is the gas constant, and T is the absolute temperature.

FOAM RHEOLOGY

The case of foam formation depends not only on the elasticity of the lamellae but also on the elasticity of the adsorbed layers. The surface rheology obviously has a great influence on the rate of relaxation of the stresses in lamellae. The most obvious effect of viscosity is to retard drainage and disturbances of any kind in the lamellae.

Plateau (*8*) first introduced the term *surface viscosity* in an experiment of damping an oscillating needle. A number of methods have been developed to measure the shear properties of interfacial films. Davies and Rideal (*9*) and Joly (*10*) have reviewed these methods. Der Vichian and Joly (*11*) and Harkins and Meyers (*12*) developed a classical canal method which is based on the flow characteristics of a liquid in an open canal. Harkins and Kirkwood (*13*) developed a relation for calculating the Newtonian surface viscosity from observed surface flow parameters. For non-Newtonian films, Mannheimmer and Schechter (*66*) reported a method which depends on surface rheological properties and provides absolute values for the surface viscosity. It also gives the yield value for either insoluble monolayers or adsorbed films.

The structural mechanical properties of the surface layers in solutions of saponin have been studied by various workers (*14*). Trapeznikov (*14*) has studied the rheology of liquid films. The surface viscosities of thin films are found of the order of 10^{-3} P. The rheology of surface layers is still to be explored experimentally and theoretically, since this field is in its early stages.

FOAM DRAINAGE

The stability of foam is completely dependent upon the conditions of the lamellae. The foam lamellae are subjected to the drainage of the liquid, during which process a progressive thinning of the lamellae takes place. A great deal of work has been carried out on thin films in order to understand foams and emulsions (*1*). Two types of thin films, rigid and mobile, are taken into account to evaluate the properties of transient and persistent foams.

The properties of metastable lamellae are found to be controlled by the following factors:

Laplace capillary suction
The attraction forces due to long-range van der Waals interaction
The electric double layer
The steric factor

Laplace Capillary Suction

The lamellae surfaces in foams have strong curvatures at the edges where bubbles meet. The place where three bubbles meet is known as the *Plateau border*. The pressure in the liquid at the Plateau border is lower than the pressure in the liquid of the bubble walls. This lower pressure is due to the force of gravity acting on the liquid which is raised above the bulk level. This reduced pressure exerts a suction force on the lamellae, causing a reduction of thickness. Hence, in the foams two different forces, viz., gravity and capillary suctions, are active in effecting the thinning of the lamellae.

According to the Laplace equation, this pressure difference between the two principal radii of curvature is given as

$$\Delta R = v\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{6}$$

For spherical bubbles the radii of curvature is the same:

$$R_1 = R_2 = R$$

then

$$\Delta P = 2v/R \tag{7}$$

Thus the smaller bubbles have a higher pressure than the larger bubbles. In foams containing different sizes of bubbles, an irregular foam collapse occurs. The smaller bubbles cause a transfer of gas through the lamellae by diffusion with the larger bubbles, ultimately causing all the gas to accumulate into a single bubble.

De Vries (*5*) made a study of gas diffusion in foam from oil in water. He calculated the rate of decrease of smaller size bubbles as a function of the radius of the bubbles, surface tension, thickness, and the permeability of liquid lamellae between the bubbles. The rate at which the bubble shrinks is given by

$$r_0^2 - r_t^2 = \frac{4RT}{P}\frac{DSvt}{\theta} \tag{8}$$

where r_0 is the initial value of a bubble, r_t is the radius of the bubble at time t, D is the diffusion coefficient, S is the solubility of gas per milliliter of liquid at normal pressure, and θ is thickness of the liquid lamellae.

Ross (*3*) extended the analysis of De Vries (*5*) and calculated the gas diffusion by studying the change in the interfacial area of the foam bubbles with time. The smaller bubbles are found to lose an interfacial area which is much larger than the interfacial area gained by larger bubbles on their expansion. Ross (*3*) obtained the relation:

$$A_0 - A = 16\pi \frac{RT}{P} \frac{DSvt}{\theta} = K_A t \tag{9}$$

where A_0 is interfacial area at time zero and A is interfacial area at time t.

By using Eq. (1), Relation (9) can be written as

$$V - V_0 = \frac{32\pi}{3} \frac{RT}{P^2} \frac{DSv^2 t}{\theta} = K_v t \tag{10}$$

Ross (*3*) proposed the determination of specific surface area by measuring the light absorbed on account of scattering by foam films. The relation derived by Clark and Blackman (*3*) for the loss of light on transmission and specific surface of the foam is

$$A = k(I_0/I - 1) \tag{11}$$

where I_0 is the intensity of incident light, I is the intensity of light after transmission through foam, and k is a constant.

The simplest method to determine gas diffusion could be adapted by using methods suggested by Ross (*3*) and De Vries (*5*). The gas expansion in the foam could be determined by measuring the density change of the aging foam. The volume of gas in 1 cm^3 of foam is given by

$$V = 1 - \frac{D}{\rho} \tag{12}$$

where D is the density of the foam and ρ is the density of liquid.

From Eqs. (12) and (1), Ross (*3*) obtained the relations

$$\frac{3P_{\text{av}}}{\rho} dD - 2v\, dA = 0 \tag{13}$$

or

$$(D_0 - D) = \frac{2v\rho}{3P_{\text{av}}}(A_0 - A) \tag{14}$$

Substituting the value of $(A_0 - A)$ from Eq. (14) gives

$$D_0 - D = \frac{3P_{av}}{2v\rho}K_A t$$

$$D_0 - D = K_D t \tag{15}$$

where

$$K_D = \frac{3P_{av}}{2v\rho}K_A$$

According to Eq. (12), the density of foam can be measured by taking a large volume of foam, possibly 2 to 3 liters. A container of appropriate size is filled with the foam and weighed at periodic intervals after each incremental volume of foam is created by the expansion of gas with the top carefully swept off.

Equation (15) is useful for foams where gas diffusion and the coalescence of bubbles simultaneously take place. In such conditions, Eq. (15) should hold for the dynamics of foam decay, and the plot of the change in density versus time should be linear.

In a foam containing bubbles of uniform size, there will be no interdiffusion between the bubbles except from the outermost layer to the atmosphere. This occurs to a lesser degree with the bubbles in the underlying layers, with the diffusion rate being minimal. In such foams, decay depends completely on the mechanism of film collapse. For many less stable foams, the decay has been measured by observing the rate at which a liquid is released; this empirical equation is

$$V = V_0 e^{-kt} \tag{16}$$

where V is the volume of liquid in a foam after time t, V_0 is the volume of liquid in the foam when $t = 0$, and k is a constant. Equation (16) is applicable to diverse foams of beer, saponin, and lauryl sulfonic acid, but it is inapplicable to the slow draining foams made from protein hydrolyzate.

Long-Range Interaction

The foam lamellae become thin due to the drainage caused from a difference of pressure in the Plateau border. When the drainage has reached a value where no thinning occurs, the film has a thickness of 150 Å and is called a *black film*.

Overbeek (*15*) emphasized that the forces causing the growth of the black film are van der Waals attraction forces between the molecules. Hamaker (*16*) carried out calculations on the basis of molecular interactions. Assuming molecular interaction independent of the medium, the magnitude of van der Waals energy of interaction for a molecule at a distance x from the surface of the object Q is given by

$$E_Q = \frac{-\pi N_q \tau}{6x^3} \tag{17}$$

where N_q is the number of molecules per cm^3 and τ is the London constant.

The energy of interaction between two interacting bodies A and B is given as

$$E_{\mathrm{AB}} = -\Pi N_a N_b \tau_{ab}/12x^2 \tag{18}$$

or

$$E_{\mathrm{AB}} = -A_{ab}/12\Pi x^2 \tag{19}$$

where

$$A_{ab} = \Pi^2 N_a N_b \tau_{ab}$$

The value A is the Hamaker constant, a basic property of any material and the measure of its dispersion effect. The Hamaker constant is used to determine an attractive force operating over a distance up to several hundred Å units.

In the case of lamellae, two surfaces are involved, containing a layer of liquid in between a certain thickness δ. For a system where interacting bodies are of the same material, the energy of interaction becomes

$$E = -\Pi N^2 \tau/12\delta^2 \tag{20}$$

and

$$A = \Pi^2 N^2 \tau$$

or

$$E = -A/12\Pi\delta^2 \tag{21}$$

The force of attraction between the lamellae can be obtained by differentiating Eq. (7) with respect to thickness δ of the liquid in between:

$$\Pi_{vw} = +\frac{A}{6\Pi\delta^3} \tag{22}$$

and

$$A = \Pi^2 N^2 \tau$$

Duyvis (*17*) gives the nonretarded van der Waals attraction (Π_{vw}) for a heterogeneous film in air with two hydrocarbon layers of identical thickness and an aqueous core of variable thickness δ_2:

$$\Pi_{vw} = \frac{A_{11}}{6\pi}\left[\frac{1}{{\delta_2}^3} - \frac{2}{(\delta_1 + \delta_2)^3} + \frac{1}{(2\delta_1 + \delta_2)^3}\right] - \frac{2A_{12}}{6\Pi}\left[\frac{1}{{\delta_2}^3} - \frac{1}{(\delta_1 + \delta_2)^3}\right] + \frac{A_{22}}{6\Pi}\left[\frac{1}{{\delta_2}^3}\right] \tag{23}$$

where A_{11}, A_{22}, and A_{12} are, respectively, Hamaker constants for interactions between hydrocarbons, aqueous, and hydrocarbon–aqueous molecules.

For a thick film where $\delta_2 \gg \delta_1$, Eq. (23) becomes

$$\Pi_{vw} = +\frac{A_{22}}{6\Pi{\delta_2}^3} \tag{24}$$

whereas for a very thin one, $\delta_1 \simeq \delta_2$, it becomes

$$\Pi_{vw} \simeq +\frac{A_{11} - A_{22} + 2A_{12}}{6\Pi{\delta_2}^3} \tag{25}$$

On the experimental side, Scheludko et al. (*18*) obtained clear evidence for van der Waals formula in free liquid films by using a dynamic technique. Scheludko's dynamic method produced an average value of about 6×10^{-12} ergs for nonaqueous films in air (*19*, *20*) and about 7.5×10^{-13} ergs for aqueous ones (*21*). Both values are in essential agreement with theory.

Lyklema and Mysels (*22*), using equilibrium foam films, obtained reasonable agreement between the measured film thickness and that calculated by assuming a value of about 6×10^{-13} ergs for the Hamaker constant.

Electrical Double-Layer Repulsion

The van der Waal forces normally cause a self-accelerating thinning and bursting of the film. But once the black film stage is reached, many films remain unchanged for a indefinite time. The monolayer–aqueous-core interfaces of films often bear a charge due to the unequal distribution of anions and cations between the interface and interior. A double-layer system is thus established in which the surface charge is balanced by the net charge residing in the diffuse layer of counterions that extends from the surface to the interior. In the case of very thin films, the charged surfaces come closer and set up a high osmotic pressure within the liquid layer by accumulating many counterions therein. The potential energy of the system increases since the energy barrier to local thinning provided by the charged monolayer is sufficient to stabilize the film against appreciable shocks.

Derjaguin and Titievskaya (*23*) treated the theory of electric double-layer repulsion in considerable detail as well as the electrostatic repulsion, based on the Goüy-Chapman theory. They reasoned that film thickness should decrease with an increasing concentration of an indifferent electrolyte in the system. In order to obtain the expression for electrostatic repulsion, it is necessary to decide whether the surface charge of the surface potential remains constant as two charged surfaces approach each other. With respect to films formed by an ionic surfactant, Derjaguin and Titievskaya considered the assumption of constant surface charge.

Scheludko (*24*), considering the simplest model for the structure of the diffuse part of the electric double layer, gave a relation for electrostatic disjoining pressure:

$$\Pi_{el} = 64CRT\tanh^2\left(\frac{2F\psi_0}{4RT}\right)e^{-x\delta} \tag{26}$$

where C is the electrolyte concentration, R is the gas constant, T is the absolute temperature, F is the Faraday constant; ψ_0 is the potential on the surface, δ is the film thickness, and x is the reciprocal of Debye length.

Scheludko and Excrowa (*25*) measured the thickness of the film for dilute saponin solutions containing 1 to 2 × 10^{-4} N potassium chloride using the capillary suction method. They found the dependence of the film thickness to vary inversely with the valency of the counterions.

Mysels and co-workers (*26*) measured the thickness of the aqueous films by using a hydrostatic pressure equal to the sum of van der Waals and double-layer pressures. Agreement between their theoretical values and experimental values was reasonably good, but the theoretical values were found to underestimate the thicknesses of the films.

Steric Hindrance

Corkill et al. (*27*) used the radio-active tracer technique to determine the drainage of the thin films. An addition of dodecanol to the aqueous solution of sodium dodecyl sulfate gave stable thin films. The proportions of dodecanol, sodium dodecyl sulfate, and water in the black film confirmed the existence of a mesomorphic phase. The multicompound character of a film leads to serious complications in connection with van der Waals pressure. Every component, because of the specific character of the van der Waals forces, will behave differently. In foams, if the lamellae have a multilayered structure, it will be difficult to explain the phenomenon of stability of films.

The other factor which explains the stability of thin films arises from the "steric hindrance" of closely packed monolayers. It is only mentioned in the literature as an obstruction offered by monolayers in which molecules are closely packed together and molecular cohesion prevents their separation when they are subjected to considerable pressure (*28*).

The foregoing discussion has reviewed the work carried out on the stability of the thin films and foams. Although present knowledge is quite advanced regarding the structure of thin liquid films, the various factors responsible for their stability, and the mechanism of rupture, much work in understanding the behavior of foams has yet to be carried out.

The theoretical treatment for foam drainage and foam breakage has not been taken up. The empirical relation given by Eq. (16)—$V = V_0 e^{-kt}$—is found inapplicable to slow draining foams. The equation is found to hold only for a limited portion of the total foam life. In many cases anomalies appear both at the beginning and at the end of the foam life (*29*).

In foam lamellae with a multilayered structure, the composition of each component will affect the stability of the foams. However, information on the change of components will be of great use in understanding the properties of foams.

In the films formed by nonaqueous solutions in which nonelectrostatic forces play an important role, the calculations on such forces will be of great use. Regarding very thin films (~50 Å), accurate information on the forces that determine the stability is not available. The work on rheological properties of foam is still in a formative stage. A standard method which could be used for measuring the stability of slow and fast draining foams is still to be devised.

PHASE EQUILIBRIA AND FOAM STABILITY

Recently, an attempt has been made by Ahmad and Friberg (*42*, *43*) to visualize the effect of different components on the stability of foam using phase equilibria.

In the case of thin films, the stability is found to be affected by the addition of dodecanol in the water solution of the surfactant. This condition is considered to be due to the formation of a molecular complex at the interface. Molecular complexes formed by surface-active agents with alcohol and acids have received great attention ever since McBain (*31*) and Ekwall (*30*) made their pioneering investigations.

Schulman (*32*) demonstrated the effect of molecular complexes upon the properties of interfacial films and the stability of emulsions and foams. Evidence for the existence of the complex between cetyl alcohol and an aqueous solution containing sodium cetyl sulfate is indicated by the fact that it is much more resistant to disruption by pressure than the film from either of the components by themselves. This phenomenon is one reason why a complex interfacial film around oil droplets is a better retardent to coalescence than the film from the surface-active agent alone (*33*).

Recent investigations by Friberg (*34*) on emulsion stability using phase equilibria show that liquid crystalline phases formed at the interfaces are responsible for increased stability. In the formation of the liquid crystalline phase, both solvents and the emulsifier take part. Further investigations (*35*) reveal the formation of a liquid crystalline phase even if the emulsifier and the two solvents are pure compounds, and the formation of molecular complexes appears difficult to visualize. However, the molecular complexes are not found to play any important role in stabilizing the emulsions and foams, as suggested by Schulman (*36*) and Sanders (*37*).

The results given by Friberg et al. rationalize the problems regarding changes of emulsion stability (*38*), viscosity (*39*) with emulsifier concentration, and the difference of emulsional behavior when different hydrocarbons are present (*40*).

A theoretical treatment of the van der Waals interactions between the emulsified droplets covered with a liquid crystalline phase was given by Friberg (*41*). The magnitude of the Hamaker constant of the liquid crystalline phase was found to be a more important factor for emulsion stability than the thickness of the adsorbed layer of liquid crystalline phase on the droplet.

The investigations made by Friberg et al. on the stability of emulsions utilizing the phase equilibria, in defining the changes in the properties of emulsions, have motivated the present researcher to study the properties of foams.

Ahmad and Friberg (*42*, *43*) have done some work on foams and have found that the phase equilibria is of great importance in giving rules for foam stabilizers and antifoaming agents. The liquid crystalline phase formed in a three-component system is found to be situated at the interface in a multilayer and to produce stable foams when it is in equilibrium with aqueous and nonaqueous micellar solutions (*42*). The liquid phases, which alone contain molecular complexes, are not found to produce stable foams.

In foam lamellae with a multilayered structure, the composition of each component of the multilayer is important in determining the stability of foams. The optimum amount of liquid crystalline phase is found to be important in producing stable foams (*43*). A study on foam using a nonionic emulsifier (EMU 050), hexadecane, and water has been carried out, and a model has been given for the stable foam where long-range van der Waals forces and steric hindrance are present (*65*). The stable foams formed by a nonionic emulsifier, hexadecane, and water system are slow draining. The empirical relation given by Eq. (16), $V = V_0e^{-kt}$, is found inapplicable in the earlier and final stages of a foam with slow drainage.

These anomalies must be investigated thoroughly. The drainage of the liquid films has been found to be greatly affected by gravity in the beginning. Gibbs (*44*) considered this effect important in bringing changes in liquid films.

In a stable foam, when a large amount of liquid is drained out, a small amount of liquid remains in the foam and foam collapse starts. The film collapse rate may be slowed down by the accumulation of stabilizing material that falls from the collapsed foam onto the remaining liquid films. Under these conditions the foam may stop breaking short of the thermodynamic equilibrium. If we consider a block sliding down a sloped surface (with sliding being frictionless), the block will end up at the lowest point, the equilibrium position. But if there is friction between the block and the surface, the block may end up short of equilibrium. Analogously, the breaking of foam which stops short of the thermodynamic equilibrium will have a rate equation with a resistance term. If we consider the breaking of foam irreversible, then the rate equation for foam breaking which does not go to completion is

$$-\frac{dV_t}{dt} = KV_t - Q \tag{27}$$

where V is the volume of foam left in the column at time t.

When $dV_t/dt = 0$, we find that $Q = kV_e$ (where V_e is the foam volume stop breaking before reaching the thermodynamic equilibrium). Therefore,

$$-dV_t/dt = K(V_t - V_e) \tag{28}$$

on integrating

$$-\int \frac{dV_t}{(V_t - V_e)} = k \int dt$$

we obtain

$$-\ln(V_t - V_e) + C = kt \tag{29}$$

where C is an integration constant when $t = 0$ and $V_t = V_0$.

$$C = \ln(V_0 - V_e)$$

$$-\ln(V_t - V_e) + \ln(V_0 - V_e) = kt \tag{30}$$

$$-\ln\left(\frac{V_t - V_e}{V_0 - V_e}\right) = kt \tag{31}$$

The above equation is used for the foam formed by a nonionic emulsifier (EMU 050) which is very stable and which stops breaking after a certain time due to the accumulation of stabilizing material (*65*).

FOAM IN CHEMISTRY AND CHEMICAL ENGINEERING

A great number of chemical reactions are conducted through the interaction between a vapor and a liquid phase. The success of reaction efficiency, rate of reaction, yield, etc. depends greatly on the contact between these phases. The factors that determine the fate of the reaction are mass transfer and heat transfer to or from the system in order to achieve the proper energetic conditions for the reactions. These operations are generally carried out in packed columns, but a foam bed reactor in gas adsorption operations offers advantages over the packed columns. The special features of the foam bed reactors are: (a) high gas–liquid interface per unit volume of the bed, (b) larger contact time, and (c) the low pressure drop.

A transport phenomenon is associated with foam generation. However, much work has been carried out regarding the mass transfer, with and without chemical reactions at the bubble surfaces (*48*). The mass transfer associated with chemical reactions in the bubble reactors has been studied by Johnson et al. (*49*). Maminov and Mutriskov (*50*) demonstrated a decrease of the mass transfer coefficient in foam layers with increasing foam height. The mass transfer in the foam layer is completely controlled by the molecular diffusion. Tien and Garbarini (*51*) showed that a decrease in the mass transfer at the foam surface is a function of time. By studying the effect of different organic additives on the mass transfer of oxygen in air–water and sodium carbonate solution through the use of a foam reactor, Zieminski and Lessard (*52*) showed that the coalescence of the bubbles decreases with an increase in the mass transfer of oxygen.

Few reports are available from experimental and theoretical investigations of the vaporization or evaporation of foam bubbles (*53*). Tarat et al. (*54*) studied the heat transfer from a single surface in a foam layer, reporting that the heat transfer coefficient decreases with an increased viscosity and a decreased thermal conductivity of the foam. An increase in temperature of a system increases the heat transfer coefficient.

By studying the bubble dynamics in foams, Wace, Alder, and Banfield (*55*) calculated the bubble residence time or drainage as a function of the surface concentration from Γ_2:

$$t = \frac{k}{h_m}\int_{\Gamma_1}^{\Gamma_2} \frac{d\Gamma}{\Gamma_e - \Gamma} \tag{32}$$

where h_m is the mass transfer coefficient given as

$$H_m = \frac{D}{d}(A + BN_{\mathrm{Re}}{}^{n}N_{\mathrm{Sc}}{}^{1/3})$$

The height of the liquid required to provide the bubble residence time is given by

$$H = Ut \tag{33}$$

FOAM FRACTIONATION AND OTHER EXTRACTION PROCESSES

Foams have been utilized by chemists, biochemists, and chemical engineers in fractionating various organic and inorganic materials from dilute aqueous solutions (*2*, *45*). The basic principle of the selective adsorption is seen in the adsorption of one or more solutes on the surfaces of gas bubbles which rise through a solution. The recovered foam is relatively rich in material which is adsorbed at the surface. The adsorption at the gas–liquid interface under equilibrium conditions is given by Gibb's relation (Eq. 5).

A comparison of foam separation with other extraction and ion-exchange processes can be made on the basis of the principle of selective adsorption.

Wace et al. (*56*) considered the foam to be a mobile ion exchange medium of low exchange capacity (about 10^{-5} equiv/ml of foam, assuming a monolayer of the surfactant on a bubble of 1 mm diameter), based on the coadsorption of ionic surfactant.

Wace et al. measured a comparative ion-exchange equilibrium for cations of various valencies by using foam with anionic surface-active agents, ion exchange, and solvent extraction methods. The foam process is found to exhibit a maximum extractability for divalent ions. Thereafter, the higher the valency, the worse the extraction.

Absorption and extraction are common processes which may be used in treating liquids with gas or vapor (*57*). Either can be carried out in a tower fitted with plates or packing selected to provide the required contact surfaces. The design of these processes is determined by the prevailing equilibrium conditions between the liquid and the gas as they progress through the tower. In most respects, similar conditions are found to prevail in the foaming process which is employed for the removal of organic and inorganic solutes from solutions.

There are several ways to describe the absorption and extraction processes, but most common are the plate efficiency, the height of the packing equivalent to one theoretical plate (HETP), and the height of the transfer unit (HTU).

Rose and Sebald (*58*) described a process for the treatment of effluents from a pulp mill by using a foaming technique. In the process which these investigators used, the concept of transfer units, they calculated HTU as a function of F/A, the liquid flow rate, and G/A, the gas flow rate. The HTU is calculated from the relation:

$$\text{HTU} = \frac{ha/(ha + h)^{1.6}h}{\ln(x_1/x_2)} \tag{34}$$

and

$$\text{HTU} = a(F/A)^2 + b(F/A) + c \tag{35}$$

where ha is atmospheric pressure, h is the height, and x_1 and x_2 are the concentration of the liquid influent and effluent, respectively.

Lemlich (*59*) described the different methods for determining the surface adsorption (Γ) experimentally, using an analogy between a foam fractionation and a distillation column. The calculations were made using different modes of operations for foam columns. These include stripping, further purification of the pool, enriching or refluxing, and further concentration of the overhead flow.

In the treatment of foam fractionation, analogous to distillation with entrainment, Lemlich considered the bubble surface to correspond to the vapor and the rising interstitial liquid to the entrainment. He employed transfer units in equations for an upward flow and downward flow, respectively, in calculating the number of transfer units. The equation for the number of transfer units for an upward flow is:

$$\mathrm{NTU} = \int_{C_w}^{C_q} \frac{dC}{C_w - C} \tag{36}$$

where C is the effective upflow concentration, C_q is the concentration in the foamate, and C_w is the concentration in the liquid pool.

In treating the foams with a surfactant where micelles are formed in the column, careful consideration must be given to the foam fractionation process because Gibb's equation (Eq. 5) does not hold good above the critical micelle concentration. What must be changed, therefore, are the equations taken into account by Lemlich (*59*) in determining the surface adsorption for different modes of operations for foam columns. In this case, however, a trial-and-error analysis is often used (*59*).

FOAM FRACTIONATION PROCESS

Grieves et al. (*60*, *61*) used a simple mass balance model for solutions containing surfactants and utilized a foam fractionation process in treating the waste streams. The mass balance was established between the feed and the foamate and raffinate streams in order to describe the performance of the process. The material balance for a batch operation is

$$V_i = V_f + V_r$$

or

$$x_i V_i = x_f V_f + x_r V_r \tag{37}$$

where V_i is the initial volume of the liquid for each batch experiment, V_f is the volume of the foam, V_r is the volume of the residual liquid, and x_i, x_f, and x_r are the concentrations of the solute in the initial liquid, in the foam, and in the remaining liquid, respectively.

The batch operation is considered to be a nonsteady-state operation, with the liquid level in the column and the foam height, together with the liquid column volume V_r and concentration x_r, changing with time. The continuous flow process overcomes all these difficulties and is considered to be a steady-state process.

Grieves et al. regarded the continuous foam operation as a multistage or multicontact mass transfer operation and applied equations in analogy to distillation, gas absorption, and extraction processes. The equilibrium relation $Y = Y(x_B)$ (where Y is the concentration of the surfactant in the liquid volume dV, and x is the concentration in the drain stream) is taken by considering the column height as equivalent to an equilibrium stage. Taking the foam column as a number of equilibrium stages, the material balance throughout the column for the continuous process is

$$L = F + B$$

or

$$x_L L = x_f F + x_b B \tag{38}$$

where L is the flow rate of the feed, F is the flow rate of the foam stream, B is the flow rate of the bottom or effluent, and x_L, x_f, and x_b are the concentrations of the solute in the feed, foam, and effluent streams, respectively.

GAS CLEANING BY FOAM METHOD

Foam fractionation processes are widely used for treating waste water and for recovering the nonsurface active material from the waste stream. Contaminated air is generally purified by bubbling through a suitable liquid. Air cleaning using foam has not attracted considerable attention because of less theoretical information. In the bubbling process the total surface area per unit volume of bubbles is less than in the case of foam. In addition, the surfaces of the bubbles present in the foam are renewed more rapidly than those of bubbles rising freely through a liquid because foam bubbles are continuously destroyed and reformed, thus providing a new, clean film surface in contact with the gas. The pressure drop of foam-type equipment is considerably less than that of bubble-type equipment.

Pozin and co-workers (*62*) described the basis of foam gas cleaning processes. They also described different techniques and designs of the processes (*62*).

As Pozin et al. (*62*) pointed out, the conditions for a stable foam are that a liquid must have a surface tension of 85 to 90 dynes/cm and a viscosity of up to two Stokes. The equipment used for gas cleaning by foam is a downward flow, overflow-weir and venture-type. The equipment is usually circular with a cross section of 4 m^2. One to eight plates are used in a single unit with larger spacings to provide higher foam heights.

In order to make a comparison of efficiencies between foam-type and other type equipment, one must have knowledge of the conversion in the foam reactors; Pozin does not give any mathematical model for predicting efficiency or conversion in the foam reactors. In the following, an attempt is made to develop a model based on the dodecahedron structure of foam in order to predict conversions in a foam reactor (*63*).

In a batch process where a shallow pool of liquid is to be foamed, the liquid enters through an inlet and falls over a perforated plate. The contaminated air flows through the perforated plate, thereby causing the falling liquid to foam. The broken foam on the top of the foam bed releases the liquid, which flows back to the liquid pool through the Plateau borders. The reacted gas leaves the column through the outlet. Foam can be considered a system consisting of a storage vessel from which foam is generated by passing gas in such a way that the liquid returning to this liquid pool is again foamed.

The material balance for the reactant in the storage vessel yields

$$\frac{-VdC_A}{dt} = QC_A - QC_A{}^1 \tag{39}$$

where C_A is the concentration of the liquid reactant in the foam, $C_A{}^1$ is the average concentration of feedback liquid, V is the storage volume, and Q is the volumetric rate of liquid going to foam.

Since no liquid is assumed to be entrained from the foam, the amount of liquid entering the foam is the same as the amount draining back into it through the Plateau borders.

To solve Eq. (39), the average concentration $C_A{}^1$ must be expressed in terms of C_A and the contact time:

$$C_A{}^1 = f(t_c, C_A) \tag{40}$$

The calculation of $C_A{}^1$ requires certain assumptions: (a) foam bubbles do not undergo either back mixing, coalescence, or change in size; (b) the reaction takes place in the films, whereas the drainage occurs through the Plateau borders; and (c) no reaction is assumed to take place in the Plateau borders. The average concentration ($C_A{}^1$) of the returning liquid is assumed to be the mean of the concentration in the storage vessel and that of the liquid at the top of the bed which has had contact with the gas for time t_c.

The concentration of the unreacted liquid reactant on the top of the foam bed is given by

$$(C_A)_{t_c} = (C_A V_1 - 2XN_{t_c})/V_1 \tag{41}$$

where X is the number of moles of liquid converted for 1 mole of reacting gas; N_{t_c} is the total amount of gas, both free to diffuse to the atmosphere and immobilized in half the film at time t_c; and V_1 is the average volume of the film.

The average concentration $C_A{}^1$ can be obtained according to

$$\begin{aligned} C_A{}^1 &= \frac{C_A}{2} + \frac{(C_A)_{t_c}}{2} \\ &= C_A + \frac{XN_{t_c}}{V_1} \end{aligned} \tag{42}$$

Substituting expression $C_A{}^1$ in Eq. (39), we have:

$$-\frac{dCA}{dt} = \frac{YQN_{t_c}}{VV_1} \tag{43}$$

Solving Eq. (43) with boundary conditions at $t = 0$, $C_A = C_{A_0}$, we obtain:

$$C_A = C_{A_0} - \frac{(XQN_{t_c})t}{(VV_1)} \tag{44}$$

The extent of the contaminated air can be determined if the concentration of the reacting liquid (C_A) at different times is known. A plot between C_A and time t will provide a straight line with slope XQN_{t_c}/VV_1. The important factor which governs the properties of the foam is N_{t_c}. This equation can be solved by taking the reaction between a liquid film surrounded by a well-mixed but definite amount of gas.

Kumar (*63*) gives the solution of this parameter for a liquid film resistance by considering a first-order reversible reaction and solving the following differential equation:

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} - \frac{ds}{dt}$$

where

$$ds/dt = \lambda c - \mu s$$

at the boundary conditions:

$$t = 0 \qquad -a < x < a \qquad s = c = 0$$

$$t > 0 \qquad x = \pm a \qquad \frac{dc}{dt} = \mp D\frac{dc}{dx}$$

where c is the concentration of the reacting gas free to diffuse inside the film, s is the concentration of the immobilized reacting gas, λ is the rate constant for the forward reaction, and μ is the rate constant for the backward reaction.

$$\frac{N_{t_c}}{N_\infty} = \left[1 - \sum_{n=1}^{\infty} \frac{\exp(p_n t_c)}{1 + \frac{a}{2} + \frac{pn}{2DK_{n^2}} + \frac{pn^2 1a}{2D^2 K_{n^2}}}\right]$$

If the resistance is in the gas phase and the foam unit is assumed to be spherical, then we have the following expression for N_{t_c}:

$$N_{t_c} = N_\infty \left[1 - \frac{6}{\Pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{Dn^2 \pi t_c}{{r_b}^2}\right)\right]$$

where n is the number of spherical units, D is the diffusion coefficient, r_b is the radius of the bubble, and N_∞ is the total amount of gas, both free to diffuse and immobilize in half the film after an infinite amount of time.

SUMMARY

An extensive investigation has been carried out in order to explain the stability and breakage of thin films. A knowledge of foam formation and destruction will permit an understanding of the various disperse systems, viz., foams, emulsions, colloidal suspensions, polymolecular adsorptions, floatation, and aerosols. However, thin liquid films provide an experimental system for studying fundamental problems concerned with the nature and range of action of the surface forces (*39*, *40*). The study of liquid films will provide a test for the theory of molecular forces of the London-dispersion type and the theory of an electrical double layer.

The foregoing discussion reviews the various investigations and possibilities of future work in order to understand the various forces which are operative in the stability of foams. Kitchener (*28*), Sheludko (*18*), De Vries (*5*), Rubin and Gaden (*2*), Bikerman (*45*, *64*), Mysel (*46*), and Clunie (*47*) have all discussed in detail the behavior and applications of thin films and foams.

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