Study of the Foamability of Solutions Using the Tensiolaminometric Technique[1]

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Abstract

The work involved in the formation (extension and contraction) of a liquid lamella inside a rectangular wettable frame has been used to study the foaming properties of aqueous solutions. Force versus displacement curves are recorded. From these curves the dynamic and the static surface tension can be calculated and the rate of adsorption of the surface-active agent can be estimated. Foam stability appears to be related to 1) the difference of work involved in expanding and in contracting the liquid lamella, 2) the rate and the irreversibility of adsorption of the surface-active material, 3) the rate of spreading of the adsorbed molecules, 4) the rate of evaporation of the solvent and 5) the rate of drainage.

The instrument can also be used to study the oil-water interface and to serve as a screening device for foaming agents and emulsifiers. Substituting solid blades for the frame offers a possibility to study wetting and dewetting phenoma (4).

Introduction

FOAMS HAVE MANY INDUSTRIAL applications, but most of the tests proposed to study them give only an overall property of the foam without explaining any mechanism. It seems desirable to determine measurable quantities upon which the foamability of a solution depends. In any study of the foamability of surfactant solutions, two main properties must be distinguished: first, the ease of formation of thin liquid lamellae which form the walls of the gas bubbles, and second, the stability of these lamellae.

The first property depends upon the lowering of the surface free energy by the adsorption of the dissolved surface-active agents at the air-water surface. The second is a function of the behavior of the lamellae during aging as they change both in surface structure and in interlaminar liquid composition. These changes largely determine the work opposing surface reduction. However, it should always be kept in mind that a foam can never be thermodynamically stable since any disappearance of surface corresponds to a decrease in the free energy of the system. Stability is achieved by creating an energy barrier which opposes surface reduction and the thinning of the foam lamella, such as increased surface viscosity, electrostatic repulsion between both sides of the lamella and so forth.

Description of the Tensiolaminometer

Two decades ago, following the pioneering experiments of Thibaud and Lemonde (1), Matalon (2,3) designed an apparatus which provides a measure for both the ease of foam formation and its subsequent stability. It essentially measures the work involved in the formation of liquid lamellae as well as in their surface reduction. The apparatus consists of a wettable wire frame inside which a liquid lamella is formed when the frame is pulled out of a solution. Actually the frame is fixed and the solution can be lowered or raised with the help of a movable table. This up-and-down movement of the table is achieved by a system of gears powered by a variable speed motor (Fig. 1). Matalon measured the force acting upon the frame, which is by definition the surface tension, with the help of a horizontal torsion balance as a function of the displacement of the frame. The torsion of the wire was determined optically and the luminous spot recorded photographically. This apparatus presents two major disadvantages: 1) a correction of the coordinates due to the torsion of the wire is needed, and 2) the optical system gets easily out of focus and is nowadays obsolete.

In our setup, the force is measured with a transducer (Sanborn C°, Waltham, Mass.) and recorded electrically. An inertia-free recorder, such as a Honeywell Visicorder, with a negligible time lag, is used since the phenomena to be measured occur quite rapidly. With a frame width of 2 cm, the surface tension can be measured within ±0.25 dynes/cm. The rate of film formation could be varied from 0.08 to 0.8 cm^2/sec.

Procedure

The frame is completely immersed in the solution and the solution is then withdrawn. As long as the frame is entirely submersed no force is acting on the frame. (The wire is so thin that buoyancy and hydrodynamic effects are negligible.) When the horizontal wire of the frame reaches the surface, surface tension starts to act. A liquid meniscus is formed around the wire and once the angle formed by the plane of the frame and the liquid meniscus surface

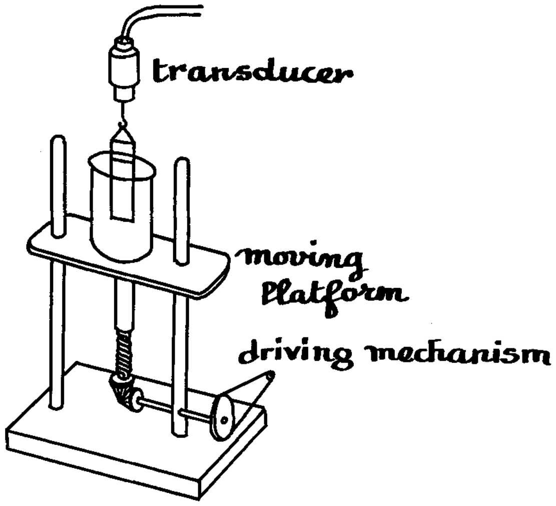

FIG. 1. Tensiolaminometer.

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[1] Presented at the AOCS Meeting, New Orleans, May 1967.

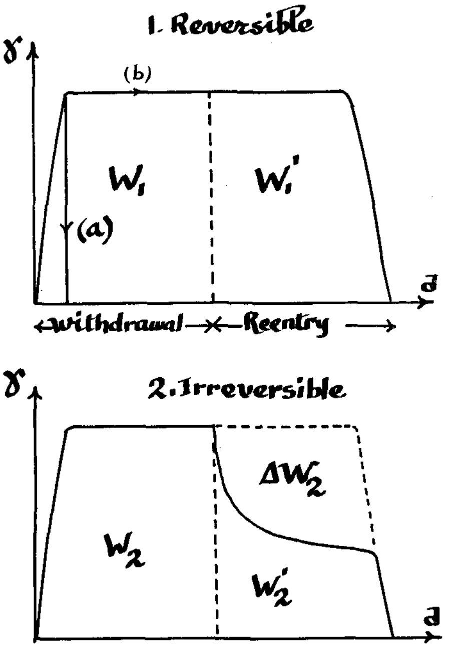

FIG. 2. Shape of the curves given by the tensiolaminometer in the case of reversible and of irreversible surface adsorption.

reaches zero, the surface tension acts vertically and two cases can be distinguished as the frame is withdrawn further:

1) In the case of pure liquids, no liquid lamella is formed and the force drops back to zero (Case a, Fig. 2).

2) In the case of foaming solutions, the force remains steady upon further withdrawal as a liquid lamella is formed inside the frame (Case b, Fig. 2). The area W_1 under the force-versus-displacement curve corresponds to the work involved in forming the liquid/air surface inside the frame. This is a direct result of the definition of surface tension as the work of surface formation. The lower the surface tension of a solution, the easier it will be to form additional air-liquid surfaces, i.e., the easier the solution will foam, assuming the liquid lamellae are stable.

In the case of a slow rate of film formation, the solution is able to feed the film and there is a constant equilibrium between the surface-active material in the bulk and that absorbed in the film. The force versus displacement curve has a horizontal plateau as the surface tension corresponds to the equilibrium value and the weight of the film is negligible.

When the rate of film formation is increased, the rate of absorption of the surface-active agents will become the controlling factor and curve A, Fig. 3, is obtained. The surface tension will always be higher than the equilibrium value, because the surface concentration of the surfactants is less than the equilibrium value. If the film withdrawal is stopped, the surface tension drops to its equilibrium value (curve B, Fig. 3). Solutions showing this type of curves tend to give stable foams, as this behavior is related to the Marangoni effect. If, because of thermal or mechanical actions, one part of the surface momentarily thins out and becomes poorer in surfactant, its surface tension increases locally and the surface tends to contract subsequently, thus bringing the film thickness to a more resistant level. This is especially the case if the surfactant concentration is not too high. At high concentrations the diffusion of the surface-active material from the bulk to the thinned section of the film exceeds the lateral diffusion in the film and no "healing" takes place.

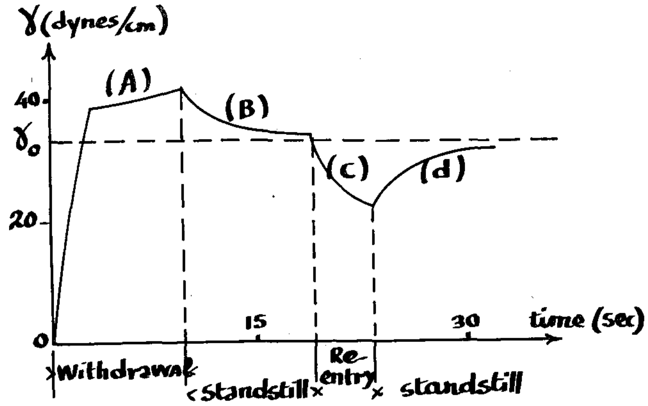

FIG. 3. Adsorption behavior showing how the dynamic surface tension values differ from the equilibrium adsorption value δ_0.

If, after the plateau has been reached, the frame is brought back into the solution, two distinct force-versus-displacement curves may be obtained. The force-versus-displacement curve upon reentry of the frame is either completely symmetrical to the curve corresponding to withdrawal or it is lower than the latter (Fig. 2).

In the first case, no change in surface tension accompanies the compression of the film, i.e., the surface-active material redissolves immediately in the bulk and the liquid lamella stays in continuous equilibrium with the bulk solution: the phenomenon is completely reversible.

In the second case, the surface-active molecules are not able to desorb from the surface as fast as the frame is immersed; they crowd together in the available surface, increasing the surface pressure with a concomitant decrease in surface tension (Curve C, Fig. 3). It is interesting to note that if the frame is stopped before complete reentry into the solution, the surface tension increases slowly to its equilibrium value (Curve D, Fig. 3). A similar curve is obtained if the surfactant substance undergoes an irreversible chemical modification at the air-water surface which renders it insoluble (e.g., proteins). The surface layer is solid in that case and can hardly be compressed.

As a general rule, solutions which give highly dissymmetrical curves form very stable foams. Foam stability is related to the magnitude of hysteresis in film expansion and contraction. A foam is subject to local mechanical and thermal stresses and the bubble walls must be able to withstand the resulting expansions and contractions. The walls must remain stable independently of the equilibrium conditions. When the stability of a film occurs only when there is equilibrium with the bulk solution, it is clear that the foam will not last.

Applications

The Efficiency of Sudboosters

The role of sudboosters is to increase the foamability and the foam stability of detergents. These sudboosters generally are only slightly soluble substances which form mixed absorbed monolayers with the detergent. This mixed compound is much less soluble and more surface-active than its components alone. It also increases surface viscosity. The be-

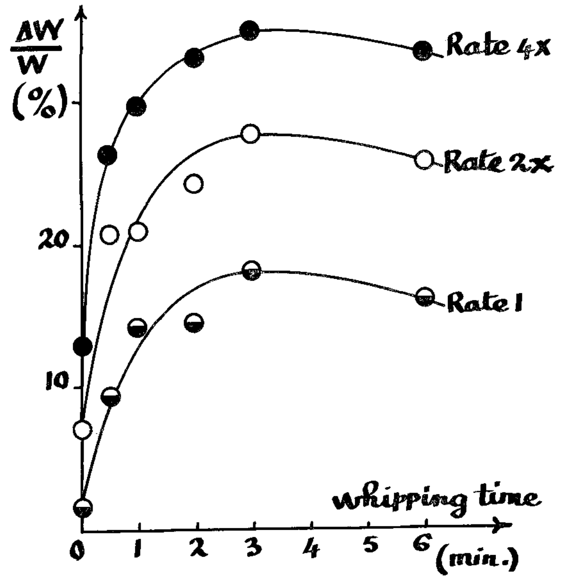

FIG. 4. Effect of the rate of lamella formation upon the relative irreversible work as a function of whipping time of a "Protein Plus" solution.

havior of a sudbooster, such as lauryl alcohol in the case of sodium-dodecylsulfate (SDS), has been examined by the tensiolaminometric technique. The addition of 0.005% lauryl alcohol to a 0.17% SDS solution lowered the surface tension from 38 to 30 dynes/cm. At the same time the work opposing surface reduction jumped from a negligible value to over 6 ergs/cm^2. The average film life increased by more than 30%.

The Behavior of Protein Solutions

A series of 50 successive caseinate films shows a marked trend towards film stability as the series proceeds. It is assumed that on contraction of the film, the excess protein is coming out as a solid phase rather than returning to the bulk. As the amount of insoluble protein in the surface increases, the film stability increases. For the last five runs of the series, the precipitated caseinate is clearly visible.

Another study on protein solutions has been done by investigating the effect of whipping time as well as rate of film formation on film (foam) stability. Film stability increases from 3 seconds before whipping to 5 seconds after half a minutes' whipping, to over 20 seconds after 1 and 1½ minutes' whipping time. Fig. 4 shows how the irreversible work changes with whipping time as well as with rate of film formation. The correlation between foam stability and irreversible work is quite striking.

Tensiolaminometric Studies at the Oil-Water Interface

As the nature of the film around the air bubbles largely determines the stability of the foam, the nature of the absorbed film at the oil-water interface determines emulsion stability. It was thus tried to form water in oil films or oil-in-water lamellae inside the frame of the tensiolaminometer. One of the difficulties encountered is the different wetting behavior of the platinum frame in the presence of emulsifiers. With emulsifiers having a low HLB value, oil-in-water films are obtained which are irreversible. These emulsifiers promote water-in-oil emulsions. A strong oil-in-water film suggests good stability, as such a film has to be broken for two water droplets to coalesce. When the HLB of the emulsifier is increased to 7, oil-in-water films are still obtained, but they are now completely reversible. The emulsion corresponding to that HLB value is of poor stability. At higher HLB values it was not possible to get reliable measurements because of wetting problems presented by the wire and too low interfacial tensions.

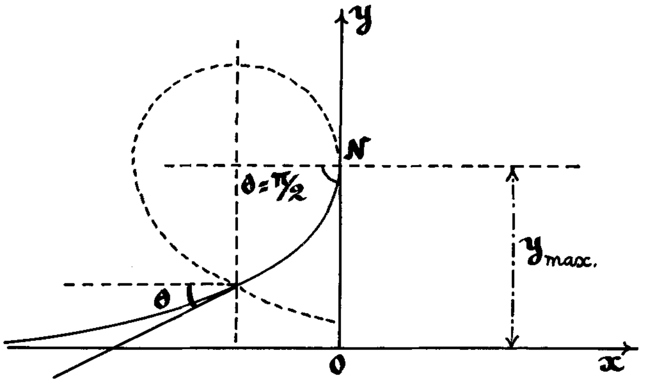

FIG. 5. Shape of the liquid meniscus serving as the basis for the calculations given in the appendix.

ACKNOWLEDGMENTS

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Appendix

The rectangular frame is assumed to be completely wettable by the liquid and to have a negligible thickness. The following relationships have been established (Fig. 5):

1) *Relationship between the position of the frame and the angle at the top of the meniscus.*

$$y^2 \rho g = 2\delta\,(1 - \cos\theta)$$

ρ = specific gravity, δ = surface tension

At the point N (vertical plane) $\theta = \frac{\pi}{2}$

$$y_{max} = \sqrt{\frac{2\delta}{\rho g}}$$

For water $\delta = 77.5$ dynes/cm,
For ethanol $\delta = 25$ dynes/cm,
$\rho = 1.00$ g/cc
$\rho = 0.79$ g/cc
hence y = 5.4 mm (at 20C)
y = 3.5 mm

2) *Relationship between the acting force F and the angle at the top of the meniscus.*

$$F = V \rho g = 2\delta \sin\theta$$

V = volume of liquid in the meniscus for a frame 1 cm wide $F_{max} = 2\delta$

3) *Relationship between F and y.*

$$F = \sqrt{2\delta\rho g} \times y\sqrt{2 - \frac{y^2}{a^2}}$$

$$\text{where } a = \sqrt{\frac{2\delta}{\rho g}}$$

$$\left.\frac{dF}{dy}\right|_{y \to o} = 2\sqrt{\delta\rho g}$$

This relationship indicates that the slope at the origin of the curves F versus y is a function of the surface tension of the solution. This can be used in the case where one wants to calculate the value of the surface tension for different rates of increase of the liquid surface.

4) *Work necessary to lift the meniscus above the liquid surface.*

It can be shown that the work W necessary to lift the meniscus above the liquid surface is the sum of two terms:

a) the work P against gravity for raising the liquid into the meniscus

$$P = 2\sqrt{2}\, a\, \delta \left(\cos\frac{\theta}{2} - \frac{2}{3}\cos^3\frac{\theta}{2} - \frac{1}{3}\right)$$

b) the work against the surface cohesion of the liquid while increasing the liquid-air interface:

$$S = 2\sqrt{2}\, a\, \delta \left(1 - \cos\frac{\theta}{2}\right)$$

$$W = P + S = \frac{4}{3}\sqrt{2}\, a\, \delta \left(1 - \cos^3\frac{\theta}{2}\right)$$

When the meniscus reaches its maximum height $(\theta = \frac{\pi}{2})$ the total work required to raise the frame becomes 2δ (for a frame of unit width), for the only work remaining will be capillary work.

Note: The detailed calculations will be provided by H. L. R. upon request. Instructions for constructing the frame can also be furnished.