FOAM FORMATION AND FOAM STABILITY

By R. MATALON, Ing.Dr., Ph.D.*

THE STUDY of foams has attracted a great number of scientists and technicians. Fundamental research was carried out in order to investigate the mechanical properties of the stabilising layer responsible for the lifetime of laminæ and bubbles along the foam column. As a result of this investigation it is now possible to increase or decrease the foam stability.

A large number of industries are interested in this foaming property. Increase in foam volume and foam stability is sought by the soap and detergent manufacturer and by the cosmetic chemist, in various branches of their industries. Laundry powders, liquid soap, shampoos, shaving creams, etc., are formulated to have a common feature of foam abundance and foam stability.

Foam production is also aimed at in many other industries, such as in the manufacture of aerated chocolates, meringues, etc., and in the production of cellular concrete for building materials.

One very useful application of foam production is undoubtedly in fire extinguishing materials. Here the foaming agent produces a very dense foam of great stability to heat. Essential components of fire-fighting foams are hydrolysed blood protein tanned with various metal ions such as ferric chloride, etc.

Foams also constitute an important item in the beer industry and the brewers are interested in keeping a good head of foam in the glass.

It follows that foams play an important and useful role in several industries. They are also very attractive, and the production of multicoloured bubbles using a pipe, a tube or a ring is an amusing pastime for children. Bubbles have been lately used for publicity purposes as well as on the stage.

On the other hand, foaming constitutes a nuisance in several industries, for example, in vacuum distillation and in fermentation, causing the vats to overflow. In the photographic paper industry, the tendency of gelatin to produce bubbles on the paper results in a non-homogeneous deposit of the silver bromide emulsion and in the appearance of white spots. Hence a great number of "antifoams" are now proposed, to overcome foaming when it is undesirable.

---

* Chemistry Department, King's College, University of London.

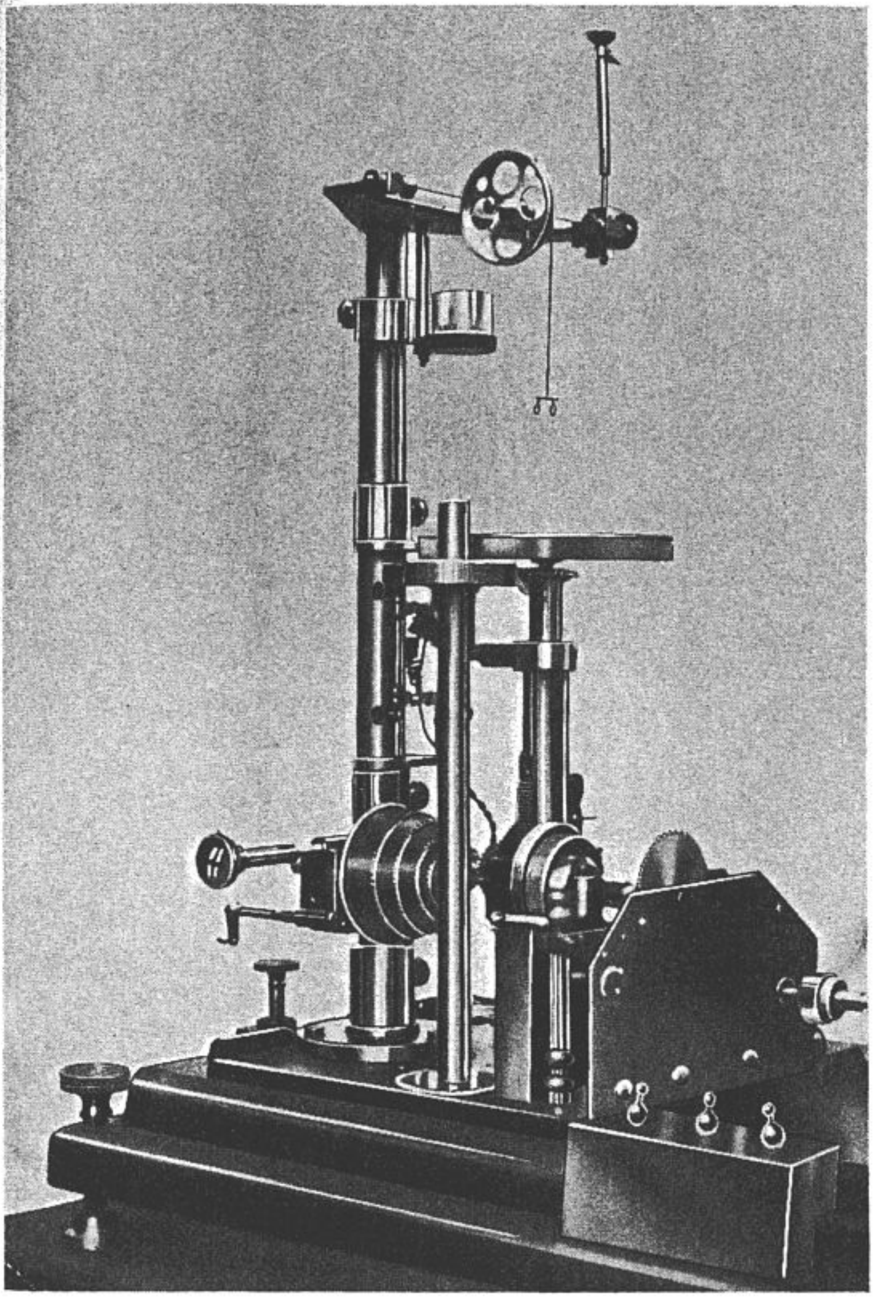


Figure 1. Torsion head and driving mechanism of the author's automatically recording apparatus for producing traction and retraction curves.

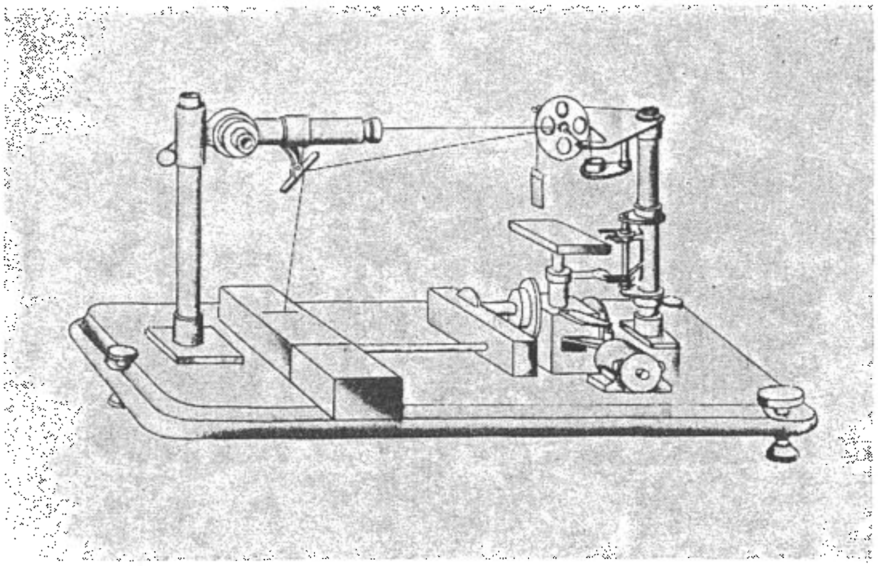


Figure 2. Schematic representation of the essential parts of the author's recording instrument

It appears that the study of foam formation and foam stability is of great importance to the industrial chemist. It is also an interesting field of study to the surface chemist. Indeed, molecular orientation in the film stabilising layer, the viscosity and plasticity of this layer, the rate of adsorption of the molecules from the bulk solution to the surface phase, and the rate of desorption from the surface layer, are factors controlling foam formation and foam stability.

METHODS FOR STUDYING FOAMING

In the following paragraphs, the various methods proposed for the study of foaming are briefly discussed.

The direct techniques are based on the rate of building up of a foam column by beating the solution mechanically or by blowing finely dispersed gas through it, using a sintered glass or a capillary tube. Such techniques permit the study of foam volume obtained from a given system under standard conditions, and of foam stability as defined by the rate of drainage of the interlamellar liquid and the rate at which the foam collapses.

Although it would appear that such techniques are quite suitable, the results are so much dependent on standardisation and experimental procedure that it is very difficult to draw definite correlations between foaming properties and molecular structure of the solute.

The fundamental properties connected with foaming are better understood when using indirect techniques such as surface tension measurements on a freshly formed surface, and on an aged surface, of the system under investigation.[1] Such measurements lead to the dynamic and the static surface tension respectively. The time taken by a freshly formed surface to reach equilibrium is related to the rate of diffusion of the solute from the bulk phase to the surface layer.

The mechanical properties of the surface layer may be investigated using the two-dimensional pendulum viscometer. Plateau,[2] Wilson and Ries,[3] and later on Clark[4], have used this instrument for determining the viscosity, elasticity and plasticity of the surface layer. Interesting results were obtained on aqueous solutions of saponins, Na oleate, Na stearate, proteins, and proteins tanned with polyvalent metal ions. Although this technique would appear quite simple, the results are erratic and the method is not sensitive enough to detect a change in the mechanical properties following the adsorption of surface-active agents which are known to cause extensive foaming. For example, Burcik[5] was unable to detect any change in the pendulum viscometer behaviour, using Na laurate, Na laurylsulphate aqueous solutions, from a clean water surface.

A New Technique Developed

A new technique has been developed by the author[6] which enables us to follow a significant change in the properties of such system. This technique has been applied to a wide range of amphipatic compounds, anionic, cationic and non-ionic series. Saponins and proteins were also investigated.

This technique originates from the work of Lenard[7] in 1924, who measured the surface tension of liquids by means of a rectangular wire frame. When the frame is withdrawn from the bulk of the liquid and raised above the surface, a pull is being applied. This pull increases gradually and, after reaching a maximum, drops slightly. The value then obtained is a measure of the surface tension of the liquid. An interesting feature inherent to the rectangular wire frame, as opposed to the ring, is the appearance for some systems of a region over which the frame is raised under a constant pull. When this is observed, a thin lamina forms in the plane of the wire frame. Using an aqueous solution of Na oleate, for example, this lamina is seen to display interference colours and drainage of the interlamellar liquid similar to those observed in the foam columns.

Before the rectangular wire frame technique could be applied for the study of foaming, several factors had to be controlled. It was found, for example, that the rate of withdrawal of the frame had a marked effect on the extension of the lamina. Moreover, the surface tension of the lamina was also found to vary with this rate.

For this purpose an automatic recording apparatus was designed by the author,[8] ensuring the withdrawal of the platinum wire frame under a constant rate. At the same

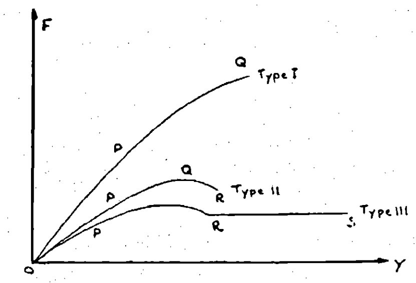


Figure 3. The three types of curves (See adjacent column.)

time the force acting on the frame was recorded on a photographic paper as a function of the displacement of the frame above the liquid surface. The traction curve was obtained during this part of the experiment. When the wire frame was returned to the liquid before breakage occurred with the surface, the variation of the force acting was then recorded on the retraction curve.

The apparatus consists essentially of a torsion head measuring device, of an optical system and of a driving mechanism. The frame is connected to a well-balanced wheel, centred on a horizontal torsion wire. The movements of the wheel are damped by attaching to it an oil damper.

The vessel containing the liquid under investigation is placed on a table, which may be moved vertically in both directions by connecting it to a motor, which drives at the same time a photographic paper. The table may be moved at various speeds by a system of gears which connect it to the motor. A light source is placed in front of the wheel and a small mirror attached to it reflects the rays through a slit on a photographic paper.

This apparatus permits the automatic recording of the force exerted on the frame by the liquid surface as a function of the height of the frame over the surface.

Figure 1 shows the torsion head and the driving mechanism, while Figure 2 represents schematically the essential parts of the instrument used by the author.

Experimental Results

1. *Low Traction Speeds*

Using low speeds of traction, i.e., 1 cm. for 10 minutes, three types of curves may be obtained depending on the System[3] (*see Figure* 3).

Type I. The frame breaks the liquid surface after a maximum pull has been applied in Q. This always occurs with a clean water surface at any speed of traction.

Type II. The force applied drops slightly after the maximum is reached, from Q to R. This occurs when the water surface is covered by an adsorbed layer, leading to a lamina of short life-time.

Type III. Along RS the force acting on the frame remains constant. This is obtained when the solution can give rise to a lamina of prolonged stability.

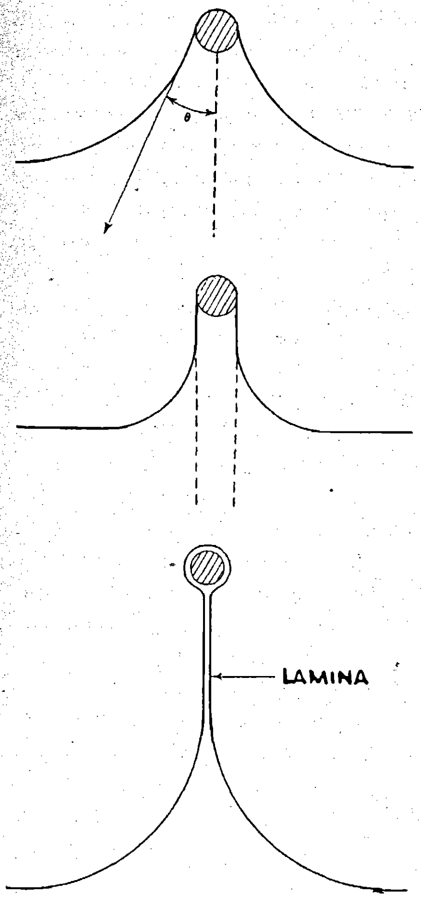
Along OPQ a meniscus[6] is formed and as θ (*see Figure* 4) decreases the force rises to a maximum till $\theta = 0$. A lamina is obtained in R and as this lamina increases in area, RS is recorded on the traction curve.

The slight drop in the force

applied in Q and R is due to the weight of liquid raised by the frame as a result of the thickness of its horizontal wire.[6]

Along RS the surface of the liquid is extended under a constant pull and the work of extending is $\gamma \ngtr S$ where γ is the force recorded along RS and $\ngtr S$ the increase in area. This demonstrates that the force recorded along RS is the surface tension of the liquid.

Figure 4. Lamina formation. (See foot of previous page.)



Using the slow traction speed (1 cm. per 10 min.) it has been possible to compare the mechanical stabilities of laminæ originated from Na oleate and Na dodecylsulphate systems. Curves have been prepared giving the results for these two systems at various dilutions.

Lamina formation is first observed in Na oleate between $\frac{M}{5000}$ and $\frac{M}{2000}$. The extension of the lamina increases steadily till a concentration of $\frac{M}{200}$ is reached, after which it decreases again. It is interesting to note that, although the surface tension remains constant for concentration above $\frac{M}{800}$, the traction curve shows that the lamina extension along RS varies greatly.

On the other hand, the results obtained for Na dodecylsulphate show that in no case is the lamina extension marked. Only very small laminæ are observed at concentrations equal or greater than $\frac{M}{600}$.

Whereas with the Na oleate it is possible to follow the slow drainage of the interlamellar liquid by observing the interference bands, with the Na laurylsulphate the draining is much more rapid. This leads to a very rapid thinning and a breakage of the small laminæ.

The fundamental difference in behaviour between the Na oleate and the Na laurylsulphate is easily found in the structure of the adsorbed layer. In the oleate system the adsorbed layer is formed by the fatty acid soap, which tends to give a liquid condensed structure, due to ion-dipole interaction between the fatty ion and the fatty acid resulting from the hydrolysis of the oleate. In the Na laurylsulphate no hydrolysis is possible and the adsorbed layer is formed by mutually repelling alkylsulphate ions.

It was found[10] that the Na laurylsulphate could lead to traction curves similar to those of the oleate system when complexing agents such as octyl or nonyl alcohol were present in the aqueous phase. Under these conditions a mixed structure is obtained in the surface layer, where the alkylsulphate chains are separated by the long chain alcohols. This results in an ion-dipole interaction which stabilises the surface structure.

Non-ionic surface-active agents, such as those obtained by the reaction of ethylene oxide on long chain alcohols, were studied in collaboration with Cohen.[11] These materials lead to prolonged laminæ stability for a particular hydrophobic/hydrophilic balance in the molecule. For an alcohol of n carbon atoms, these derivatives with n — 3 ethylene oxide lead to an extended RS portion of the traction curve. For a longer polyoxyethylene chain, the adsorbed layer is too hydrophilic and the lamina stability is markedly decreased.

2. *High Traction Speeds*

For traction speeds of 1 cm. per 10 seconds or greater, it becomes possible to characterise the mechanical stabilities of relatively unstable laminæ such as those obtained from Na laurylsulphate aqueous solution. In addition to the traction curves already described, a fourth type may be now observed where the extension of the lamina along RS occurs under increasing tension (*see Figure* 5). This is due to a lowering of the concentration of the adsorbed molecules as the surface layer is extended along RS. Type IIa is obtained with relatively dilute solutions of alkylsulphate, alkylsulphonate, alkylarylsulphonate, etc. This suggests that the adsorption of the molecules from the bulk solution is insufficient to compensate for the increase in surface area. Systems leading to Type IIa exhibit a relatively smaller foaming volume as compared with those showing the Type III traction curve.

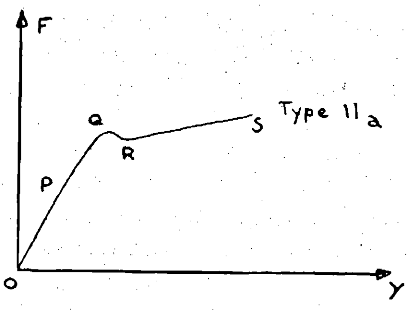


Figure 5. (See below.)

The increase in tension along RS may reach values as high as 5 dynes. The author has previously published a whole series of traction curves obtained with Na oleate and Na laurylsulphate respectively.[9] With Na oleate a lamina is first observed at $\frac{M}{2000}$. The height of the lamina increases and reached a maximum of 22 mm. at $\frac{M}{83}$, after which a further increase in concentration decreases the height of the lamina. Using Na laurylsulphate, a very small lamina is obtained at $\frac{M}{600}$. At higher concentration the lamina increases in height, reaching a maximum value of 16·6 mm. at $\frac{M}{100}$. At the same time the traction curves show that the tension rises as the lamina extends.

Traction curves studies at low and at high speeds on Na oleate and Na laurylsulphate lead to the conclusion that both reagents give rise to extensive foaming over a definite concentration range : $\frac{M}{2000}$ — $\frac{M}{100}$ for Na oleate, $\frac{M}{600}$ - $\frac{M}{100}$ for Na laurylsulphate.

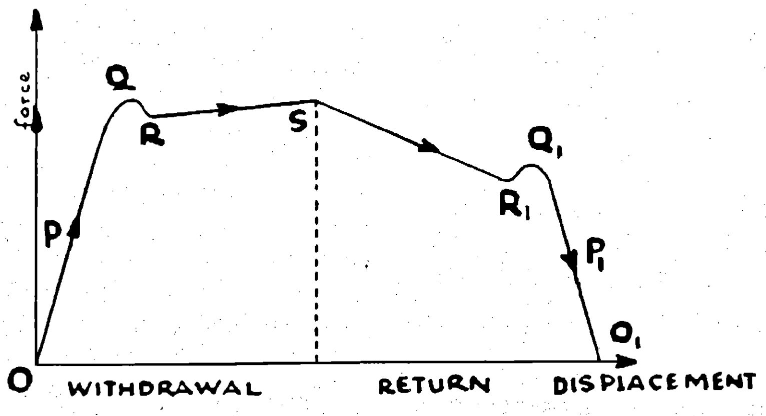
At concentrations higher than $\frac{M}{100}$ the volume of the foam decreases, presumably due to an increase in the viscosity of the solution which slows down the rate of adsorption of the molecules from the bulk phase to the surface layer.

Furthermore, traction curve experiments at low speeds demonstrate that the Na oleate foams are much more stable to drainage and thinning than those of the alkylsulphate.

Retraction at High Speeds

The retraction curve is obtained when a lamina is returned back to the liquid surface before its maximum extension. This is carried out by reversing the movement of the liquid surface so that the frame immerses in the bulk of the solution. Retraction permits the study in further detail of the properties of the surface layer. Photographic recording shows that the lamina may either behave reversibly or irreversibly.[8] In most cases, however, an irreversible behaviour is observed, the tension being markedly lowered as a result of the retraction (*see Figure* 6). The tension recorded in R_1 is markedly lower than in R. Using alkylnaphthalene sulphonate[12] the drop in tension $\gamma_R - \gamma_{R_1} = D\gamma$ may easily reach 15 to 20 dynes per cm. for the most dilute systems. As the concentration of the solute increases, $D\gamma$ decreases and tends to become zero. This is observed with Na oleate, for example, when the concentration is equal to or higher than $\frac{M}{100}$. Over this range the surface behaves reversibly on traction and retraction, as shown in Figure 7, the tension of the laminæ remaining constant, since the solution has reached its maximum surface pressure.

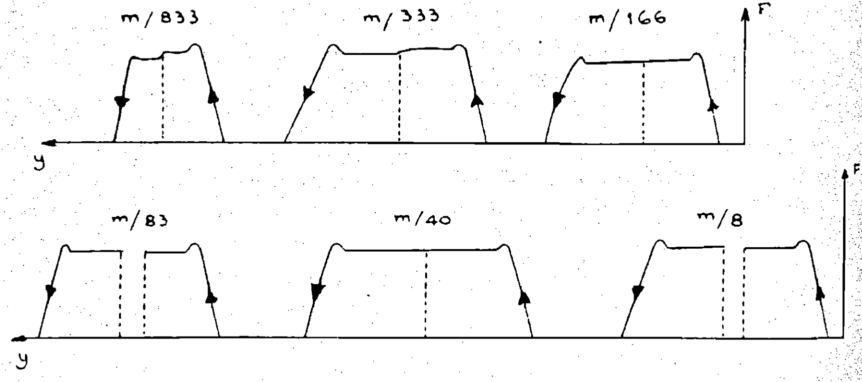
$D\gamma$ is high when the adsorbed molecules on the lamina do not easily desorb from the surface layer. Thus, on retraction, the surface concentration increases and consequently the surface tension is lowered. It appears that irreversibility is caused by the fact that the molecules present in the surface layer are in a



way insolubilised and fixed in it during retraction. This effect is one of the most important features of dilute solutions of foaming agents. In these solutions, although the dynamic and the static surface tensions are very high, stable foam columns may be obtained as a result of the compression of originally unstable laminæ. Indeed, as the foam column rises, mechanical changes are established, and laminæ of initially large surface areas are

(Continued on next page)

Figure 6 (above) : *An example of irreversible behaviour on retraction.* Figure 7 (below) : *Reversibility on traction and retraction exhibited with sodium oleate.* (See page 223.)



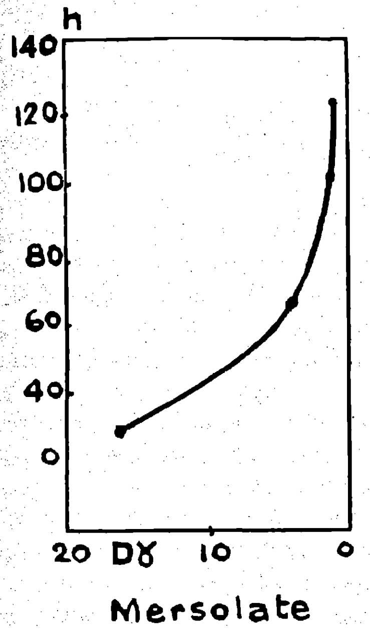


Figure 8. Variation of mersolate foam volume as a function of $D\gamma$.

retracted and stabilised by the higher surface concentration then reached. Traction and retraction at high speeds have shown that[1 2] for a given solute the foam volume increases as $D\gamma$ decreases. Maximum foaming is observed when $D\gamma = 0$. Further increase in concentration above the optimum results in decrease of foaming, due to a slowing down of the rate of adsorption. Figure 8 demonstrates clearly the variation of Mersolate foam volume as a function of $D\gamma$.[12]

CONCLUSION

The study of foaming, using direct and indirect methods, has been reviewed. The wire frame technique adapted for that study has been described in detail. Various factors controlling foam formation and foam stability, i.e., the rate of adsorption in the surface layer and the rate of desorption on compression of the lamina, have been followed, using the traction and retraction curves. Drainage of the interlamellar liquid and stability of the thinned laminæ may be easily followed on the traction curves. Stabilisation of the laminæ on compression was demonstrated on the retraction curves and it is concluded that foaming agents tend to stabilise the lamina during the retraction process.

References

[1] D. G. Dervichian. 1944. *Corps Gras Savons*, Vol. 2, No. 6, p. 164.

[2] J. Plateau. 1873. "Statique experimentale et théorique des liquides soumis aux seules forces moleculaires."

[3] R. E. Wilson and E. D. Ries. 1923. Coll. Symp. Monograph, p. 161.

[4] N. O. Clark. 1947. Chem. Research Special Report No. 161. Dept. of Scientific and Industrial Research.

[5] E. J. Burcik. 1950. *J. Colloid Science*, **5**, 421.

[6] R. Matalon. "Surface Chemistry," Butterworth, pp. 195–201.

[7] Lenard *et al.* 1924. *Ann. der Physik*, **74**, pp. 381–404.

[8] R. Matalon. 1948. *Memorial Services chimiques etat*, **34**, 345–351.

[9] R. Matalon. 1948. 15th June Dr. Ing. thesis, Lyon.

[10] R. Matalon. 1951. *The Journal of the Society of Cosmetic Chemists*, II, No. 3, p. 122.

[11] Unpublished work.

[12] M. Raison, R. Matalon. 1948. *Memorial Services chimiques etat*, **34**, pp. 353–371.