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80th anniversary

DROP DEFORMATIONS UNDER SURFACE TENSION GRADIENTS

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Abstract. The effect of the surfactant adsorption on the surface of a free liquid drop immersed in an unbounded liquid (the densities of the two bulk liquids are equal) is studied. The interfacial tension gradient caused by the surfactant adsorption at the drop surface generates surface forces exerted within the boundary region of the drop. The effect of the variable interfacial tension gives rise to a surface flow (i.e. Marangoni flow) which causes the motion of the neighboring liquids by viscous traction, and generates a hydrodynamic pressure force (named Marangoni force) which acts on the drop surface. The Marangoni force is examined on several cases using nondeformable and deformable drops.

Key words: interfacial tension gradient, Marangoni force, Marangoni effect, free drop deformations, dynamic instability, hydrodynamic model.

1. INTRODUCTION

The boundary between two phases of matter is known as the interfacial zone or, the interface. It is the thin layer surrounding a geometric surface of separation, in which the physical properties differ much from those in either of the bulk phases. The thickness of this layer is ill-defined because the variations of physical properties across it are continuous. We shall consider it as infinitely thin, i.e., as a geometric surface. Since the thickness of interface is of the order of molecular dimensions, such an approximation is justified in treating the macroscopic movements of liquids.

Under given conditions, tangential forces may exert in the interface of the two liquids, together with the normal pressure. If the surface tension σ , of the liquid interface changes from point to point, a tangential force will be exerted in addition

to the pressure normal to the surface and its magnitude is determined by the surface tension gradient, which per unit area is [1]:

$$\vec{p}_t = \text{grad } \sigma.$$

The plus sign preceding the gradient indicates that this force tends to move the surface of the liquid in a direction from lower to higher surface tension.

Surface active compounds (surfactants), present in even small quantities, have an important role in determining the hydrodynamic behavior of the two phase system. Those cases of liquid motion, in which surface tension plays an important role, belong to the interfacial hydrodynamics.

There are many examples where the presence of a surfactant has an important role. Probably, the best known is the effect of a surfactant on a liquid drop, immersed in a bulk liquid, initially at rest [2]. The force, acting on the unit volume of the drop (density ρ') immersed in a bulk liquid (density ρ), is cancelled,

$$(\rho - \rho') \vec{g} = 0,$$

when either the densities of the two liquids are equal ($\rho' = \rho$) or in the absence of gravity $\vec{g} = 0$ (zero gravity). Such a drop is called “free” and is motionless.

Free drops undergo complicated motion when a surface tension gradient is applied on the drop surface. Translational and rotational motion, oscillations, surface waves and deformations have been experimentally evidenced. To explain the free drop dynamics we have developed some experiments and theoretical models [3–6]. We have shown that the surface Marangoni flow causes the motion of the neighboring liquids by viscous traction, which generates the force of hydrodynamic pressure, named Marangoni force.

The aim of this paper is to show, experimentally and theoretically, that this Marangoni force is correlated with the surface coverage degree, namely with the extent to which the drop surface is covered by the surfactant. Our calculations have shown that this force acts like a hammer and like an engine. So, we divided this force in:

- “hammer” force, responsible with the deformation and break up of the drop, oscillations and surface waves, and
- “lifting”(propulsive) force, responsible with the translational motion of the drop.

Certainly, these results can not be attribute to a single mechanism, in our case a mechanical one, but we must consider also other mechanisms, namely, the surface dilution and tip-stretching of the surface tension, as well as capillary forces. In our opinion, the real flow at the drop interface and consequently, the Marangoni force is the principal mechanism.

2. EXPERIMENTAL MODEL

We shall consider a viscous liquid drop (in our experiments with a volume between 0.4 cm^3 and 7 cm^3 , noted L' of density ρ') immersed in an immiscible bulk liquid L , (density ρ). The two liquids having the same density the drop is motionless or at zero gravity. The two liquids inside and outside the drop are Newtonians, incompressible and viscous, having the viscosities μ and μ' . The surface between the two liquids is characterized by an interfacial tension noted σ_0 .

A small quantity of a surfactant (e.g. a droplet of 10^{-3} – 10^{-2} cm^3 , which is very small compared with the volume of the initial drop) is introduced on a well-chosen point (called injection point) at the drop surface; surfactants, also known as tensides, are wetting agents that lower the surface tension of a liquid.

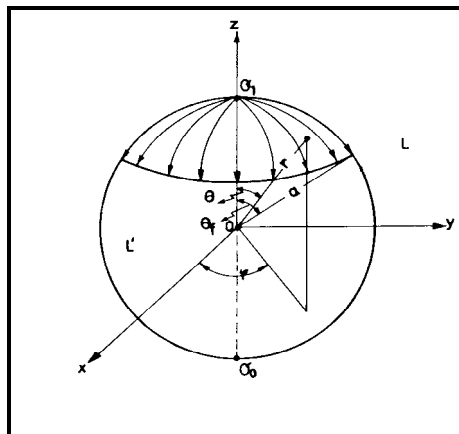


Fig. 1 – The spreading of a surfactant on a free drop surface.

The surfactant, because of its molecular structure, is simultaneously adsorbed at the liquid-liquid interface and is continuously swept along the meridians of the drop. In the injection point, the interfacial tension is instantaneously lowered to σ_1 ($\sigma_1 < \sigma_0$) value. A gradient of interfacial tension is established over the surface of the drop. Consequently, the Marangoni spreading of the surfactant takes place from low surface tension to high surface tension. We mention that local changes in temperature, in electric charge or the presence of surface chemical reactions might produce a similar effect.

The symmetry of the problem suggests a system of spherical coordinates (r, θ, φ) with the origin placed in the drop center and with the Oz axis passing through the sphere in the point of the minimum interfacial tension, *i.e.* the injection point of the surfactant. We underline that the surfactant injection point at the drop surface may be taken anywhere, the drop being initially at rest. In the following, we shall take it like shown in Fig. 1, or otherwise specified.

3. VARIATION OF THE INTERFACIAL TENSION

The variation of the interfacial tension over the drop surface must be defined before we can proceed with the analysis of the model. Generally, the interfacial tension, σ , is assumed to be distributed [7] within the surfactant invaded region, ($0 \leq \theta \leq \theta_f$), by

$$\sigma(\theta) = \sigma_m - a_1 \cos \theta,$$

where σ_m and a_1 are constants.

For the variation of the interfacial tension with θ , we have proposed for the constant values, $\sigma_m = \frac{\sigma_0 - \sigma_1}{1 - \cos \theta_f} + \sigma_1$ and $a_1 = \frac{\sigma_0 - \sigma_1}{1 - \cos \theta_f}$. Thus, the above equation becomes:

$$\sigma(\theta) = \frac{\sigma_0 - \sigma_1}{1 - \cos \theta_f} (1 - \cos \theta) + \sigma_1, \quad (1)$$

where $\sigma_0 = \sigma(\theta_f)$ and $\sigma_1 = \sigma(0)$. Eq. (1) presents the advantage that it contains the angle θ_f and permits the calculation of σ for different drop coverage with surfactant.

In Fig. 2, we give the plot of Eq. (1) for a particular case $\theta_f = \pi/2$, $\sigma_0 = 7.5$ and $\sigma_1 = 3.5$.

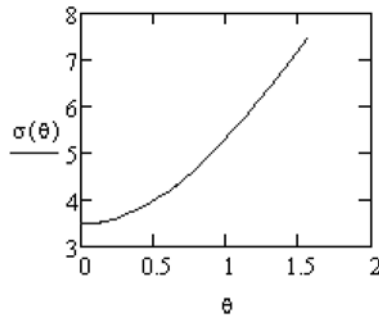


Fig. 2 – The variation of the surface tension, $\sigma(\theta)$, versus angle θ .

For the situation when the surface of the entire drop is covered with surfactant, $\theta_f = \pi$, Eq. (1) is similar to that one proposed by other authors [8]. This confirms that Eq. (1) proposed by us in its general form is correct.

Further, by derivation of Eq. (1), the interfacial tension gradient in the invaded drop region with surfactant

$$\frac{d\sigma}{d\theta} = \frac{\sigma_0 - \sigma_1}{1 - \cos \theta_f} \sin \theta, \quad (2)$$

is obtained.

The interfacial tension σ_0 is constant in any point of the uncovered drop surface, while the interfacial tension difference $\Pi = \sigma_0 - \sigma_1$ arises only in the invaded region with surfactant. Therefore, it is clear that only σ_1 and σ_0 , i. e. the minimum and the maximum values of the interfacial tension can be experimentally measured.

4. THEORETICAL MODEL

The theoretical model reported here considers that the drop is initially at rest and the real surface flow – Marangoni flow – arises on the drop surface, with a distinct front, which advances continuously; without a surfactant transfer inside or outside the drop. The drop surface is considered a two dimensional, incompressible Newtonian fluid. The Reynolds number of the inside and outside flow is less than unity.

The equations governing the flow inside and outside the drop are the continuity and Navier-Stokes equations [9-11]. The continuity equations for an incompressible fluid are for the outside and inside flow

$$\nabla \cdot \vec{v} = 0, \quad (3)$$

$$\nabla \cdot \vec{v}' = 0, \quad (4)$$

where \vec{v} is the velocity of the bulk liquid L and \vec{v}' represents the velocity of the liquid L' within the drop.

The Navier-Stokes equations for a steady flow are:

$$(\vec{v} \cdot \nabla) \vec{v} = -\frac{1}{\rho} \text{grad } p + \frac{\mu}{\rho} \Delta \vec{v}, \quad (5)$$

$$(\vec{v}' \cdot \nabla) \vec{v}' = -\frac{1}{\rho} \text{grad } p' + \frac{\mu'}{\rho} \Delta \vec{v}', \quad (6)$$

where p and p' are the pressures outside and inside the drop. All the parameters are considered constants.

We propose here to give some account on the equations governing the fluid motion in an interface, considered as a two dimensional, incompressible Newtonian fluid, having surface density Γ , surface dilatational κ viscosity and surface shear ε viscosity. Even that we have considered the interface like a bi-dimensional geometrical surface, it has a finite thickness, about 5×10^{-10} cm.

The flow in a surface is not just a flow in a two-dimensional space whose governing equations will be immediate analogs of the three-dimensional ones. In contrast with the three-dimensional space, this surface is a two-dimensional space that moves within a three-dimensional space surrounding it. In our case, the interface is the region of contact of the two liquids, namely drop liquid and bulk liquid. This is again a new feature which obliges us to take account on the dynamical connection between the surface and its surroundings, namely on the traction exerted by the outer \vec{T} and the inner \vec{T}' liquid upon the drop interface.

The equation of the interfacial flow [12-14] is

$$\Gamma(\vec{w} \cdot \nabla_s) \vec{w} = \vec{F} + \nabla_s \sigma + (\kappa + \varepsilon) \nabla_s (\nabla_s \cdot \vec{w}), \quad (7)$$

where $\vec{w} = \vec{v}_s$ is the interface velocity, $\vec{F} = \Gamma \vec{g} + \vec{T} - \vec{T}'$ is the external force acting on the drop surface and ∇_s is the surface gradient operator. Because the surface density is very small ($\Gamma \approx 10^{-7} \text{g}\cdot\text{cm}$) the inertial term can be neglected against the remainder terms. It is significant to underline that equation (7) can be used in two ways: as the equation which describes the surface flow or as a dynamical boundary layer condition.

In order to find the distributions of the velocities \vec{v}, \vec{v}' and of the pressures p, p' , the system of equations (3)-(6) must be solved taking into account some appropriate boundary conditions [9-11], for the interface between the two contiguous liquids.

The velocities of the inner and outer liquid of the drop must satisfy the following kinematical conditions:

- the outer velocity must be zero far from the drop surface,
 $\vec{v} = 0$, for $r \rightarrow \infty$;
- the normal component of the outer and the inner velocities must be zero on the surface of the drop
 $\vec{v}_n = \vec{v}'_n = 0$, at $r = a$;
- the tangential velocity components of the two liquids at the interface must be continuous:
 $\vec{v}_t = \vec{v}'_t$, at $r = a$;
- the velocity \vec{v}' within the drop must remain finite at all points, particularly at the centre of the drop ($r = 0$ the origin of the coordinates).
- In addition to these kinematical conditions, a dynamical condition must be fulfilled at the interface and is given by Eq. (7).

Eqs. (3-7) with these appropriate boundary conditions lead to the distribution of the velocity \vec{v} and of the pressures p , outside of the drop:

$$v_r(r, \theta) = \frac{A}{(1 - \cos \theta_f)} \left(\frac{1}{r^3} - \frac{1}{a^2 r} \right) \cos \theta, \quad (8a)$$

$$v_\theta(r, \theta) = \frac{A}{(1 - \cos \theta_f)} \left(\frac{1}{2r^3} - \frac{1}{2a^2 r} \right) \sin \theta, \quad (8b)$$

$$p(r, \theta) = -\frac{\mu A}{a^2 (1 - \cos \theta_f)} \frac{\cos \theta}{r^2}, \quad (8c)$$

where

$$A = \frac{(\sigma_0 - \sigma_1) a^3}{3(\mu + \mu' + 2\kappa/3a)}. \quad (8d)$$

Similarly expressions for the inner flow are obtained.

5. MARANGONI FORCE EXERTED ON THE DROP

Further, we calculate the Marangoni force exerted on the free drop due to Marangoni flow. The Marangoni surface flow give rise to a stream of liquid directed to the drop along the Oz axis.

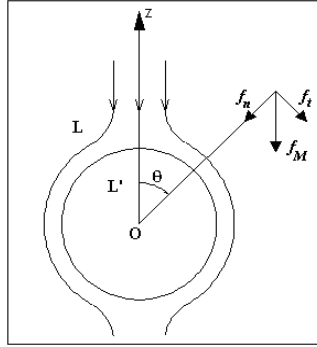


Fig. 3 – The hydrodynamic force $f_M(r, \theta)$ acting on a point.

This stream arises as a consequence of the continual replacement of that liquid layer which has been displaced by the surface flow, similar with a ventilation effect [3], as can be seen in Fig. 3. The hydrodynamic force $f_M(r, \theta)$ acting on a point may be decomposed in its normal $f_n(r, \theta)$ and tangential $f_t(r, \theta)$ components.

Immediately, it is observed that the flow occurs with the movement of the outer liquid L (Fig. 3) driven by viscosity, while the forces of hydrodynamic pressure will act on the drop L' . The resultant of the forces exerted by the fluid on the drop, F_M , due to the symmetry of the Marangoni flow, is oriented along the Oz axis. This force, acting on the drop, may be calculated from the general expression of the force [9]:

$$F_M = \iint_S \left[(p_{rr})_{r=a} \cos \theta - (p_{r\theta})_{r=a} \sin \theta \right] ds, \quad (9)$$

where S is the surface covered (invaded) with surfactant, p_{rr} and $p_{r\theta}$ are the normal and tangential components, respectively, of the viscous stress tensor:

$$p_{rr}(r, \theta) = -p + 2\mu \frac{\partial v_r}{\partial r}, \quad (10)$$

$$p_{r\theta}(r, \theta) = \mu \left(\frac{1}{r} \frac{\partial v_r}{\partial \theta} + \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r} \right). \quad (11)$$

From Eqs. (8) one obtains for the normal (Eq. (10)) and tangential components (Eq. (11)) of the stress tensor, at the drop surface ($r = a$), the following equations [15]:

$$(p_{rr})_{r=a} = - \frac{\mu(\sigma_0 - \sigma_1)}{a(\mu + \mu' + 2\kappa/3a)(1 - \cos \theta_f)} \cos \theta, \quad (12)$$

$$(p_{r\theta})_{r=a} = - \frac{\mu(\sigma_0 - \sigma_1)}{a(\mu + \mu' + 2\kappa/3a)(1 - \cos \theta_f)} \sin \theta. \quad (13)$$

The surface element in spherical coordinates on the drop ($r = a$) is $ds = 2\pi a^2 \sin \theta d\theta$. Further, after the integration of Eq. (9) by using Eqs. (12) and (13), the force, acting on the drop surface, is given by the following expression:

$$F_M(\theta) = C(1 - 2 \cos \theta_f - 2 \cos^2 \theta_f), \quad (14)$$

where

$$C = \frac{2\pi a \Pi}{3(1 + \lambda)} \quad (15)$$

and $\lambda = \mu'/\mu$ is the ratio of the bulk viscosities [16].

Normal forces acting on the interface will tend to deform the drop from a spherical shape. So, the principal mechanical factor which can modify the shape of the drop, namely deformations and break-ups of a drop, is the normal component

of the Marangoni force (Fig. 3). To understand better the role of this force, on the deformations of the drop, it will be useful to calculate the normal F_n component of the resultant force F_M .

The normal component F_n of the force F_M is given by

$$F_n = \iint_S (p_{rr})_{r=a} \cos \theta \, ds \quad (16)$$

and using Eqs. (12) and (15) and the surface element in spherical coordinates, the normal component of the force, acting on the drop surface, becomes after integration

$$F_n(\theta_f) = C(-1 - \cos \theta_f - \cos^2 \theta_f). \quad (17)$$

It can be seen that this force F_n depends on the θ_f angle, namely, on the extent to which the drop surface is covered by the surfactant, the interfacial tension difference Π and the ratio of the bulk viscosities, λ .

The normal component of Marangoni force (in short normal force) is negative and consequently acts in the opposite direction of the normal at the drop surface (Fig. 3) for any degree of coverage with surfactant. Also, it can be observed from Eq. (17) that this component is at its minimum for $\theta_f = 0$ (i.e. at the point of the surfactant injection) and increases rapidly but it never reaches positive values for any value of θ_f . The maximum magnitude of the normal force is for $\theta_f = 0$ and is given by

$$F_n(0) = \frac{2\pi a \Pi}{1 + \lambda}. \quad (18)$$

It is to be observed that $F_n(0) = F_M(0)$.

The normal force acts like a hammer (hammer effect), deforming or even breaking up the drop, for any value of θ_f between 0 and π . As shown by Eq. (18), the hammer effect appears directly proportional with Π and with the radius (a) of the drop and inversely proportional to λ .

The tangential component F_t of the Marangoni force, or tangential force, is responsible for translational motion of the drop and it is given by

$$F_t = -\iint_S (p_{r\theta})_{r=a} \sin \theta \, ds. \quad (19)$$

After the integration, F_t is given by the following expression

$$F_t(\theta_f) = C(2 - \cos \theta_f - \cos^2 \theta_f). \quad (20)$$

The tangential force F_t is positive for any value of θ_f between 0 and π , namely for any extent of coverage with surfactant on the drop surface. It is found, from Eq. (20) that the tangential force F_t is practically zero for small value of θ_f , having a maximum value at $\theta_f = 2\pi/3$.

The resultant force, $F_m = F_M/C$ and its two components, normal $F_n = F_n/C$ and tangent $F_t = F_t/C$, are plotted in Fig. 4.

The resultant force, F_m , vanishes for $\theta_0 \approx 7\pi/18 (\approx 68.53^\circ)$. It is to be noted that for any degree of coverage, $\theta_f < \theta_0$, with surfactant, the resultant F_m exerted by the external liquid upon the drop is oriented towards the negative direction of the Oz axis.

From Fig. 4, it results that for small angles of surfactant covering of the drop surface, the normal force dominates the tangent force. Consequently, the normal component of the Marangoni force induces a change in the drop shape. For the surfactant injection moment, $\theta_f = 0$, it is also observed that the following relation $F_M(0) = F_n(0)$ is obtained.

At greater surfactant coverage degree of the drop surface, at $\theta_f > \theta_0$, although F_n is not zero, the tangent force F_t is much larger than the absolute value of the normal force, so that the resultant force F_M is positive. In other words, the normal force and the tangent force do not cancel out for any value of θ_f and consequently the resultant force F_M changes its sign.

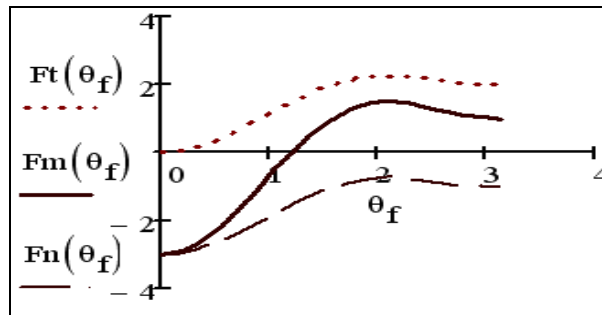


Fig. 4 – The forces acting on a drop surface.

The presence of an interface between two liquid phases may exert an influence on the motion of the bulk liquids when the surface tension varies from point to point in that interface. The modification of the surface tension is not a simply reduction of the surface tension. It involves tangential forces arising on the liquid surface, whose magnitude is determined by the surface tension gradient. The occurrence of these tangential forces in the interface always sets the interface into motion.

This movement, through the ventilation effect (Fig. 3), leads to the appearance of the Marangoni force, F_m , with its normal F_n and tangent F_t components. The normal force component causes the drop deformation and it is the dominant force, for $\theta_f < \theta_0$, and it brings the hammer effect. The tangent force component incites the displacement of the drop (such as lifting effect) and it is the principal force for $\theta_f > \theta_0$.

Finally, we wish to point out also an important factor of the hammer force as the origin of other processes. Indeed, the modification of the surface area of a drop, when the drop is deformed to a non-spherical shape, dilutes the surfactant surface concentration and the deformation of the drop is different from that expected one for the equilibrium σ_0 case. This is called the surface dilution effect. Also, surfactant molecules may accumulate at the tip of the drop due to convection, especially at the break-up process of the drop. This decreases the local interfacial tension and causes the tip to be overstretched. This is called the tip-stretched effect. When the deformations a drop get a concave surface, capillary forces also appear which tend to bring the drop into the initial spherical shape. All these deformations appear, in our opinion, only as a consequence of the hammer effect and the convective real flow of the surfactant molecules.

Therefore, we suggest that the primary effect, due to a reduction of the equilibrium interfacial tension (σ_0) in the injection point of a free drop surface with a surfactant, at $t=0$, is the appearance of a real surface flow (Marangoni flow) of the surfactant on the drop surface. This convection flow of the surfactant modifies the equilibrium surface tension, σ_0 , and a Marangoni force $F_M(\theta_f)$ will act on the drop. At the beginning it acts like a hammer which changes the shape of the drop, or break-up it and consequently, several factors might appear, namely, the surface dilution and tip-stretching, as well as capillary forces.

Using the asymptotic expansion of the function $1/1+\lambda$, when $\lambda < 1$, we may have simply an asymptotic representation for $F_M(\theta_f)$

$$F_M(\theta_f) = \frac{2\pi a \Pi(1-\lambda)}{3} (1 - 2 \cos \theta_f - 2 \cos^2 \theta_f).$$

6. EXPERIMENTAL SECTION

The experimental work on drop dynamics and Marangoni instability was performed in liquid-liquid systems of equal densities presented in Tables 1 and 2. The densities of the liquids were determined picnometrically and the bulk viscosities by using an Ubbelohde viscometer. The surface dilatation viscosity at the liquid/liquid interface was not directly measured and only a few indications concerning this magnitude for the liquid/gas interface have been found previously [3, 17].

The interfacial tension of the liquid/liquid systems was determined by a method based on capillarity and its value is given in Table 2. The measurement of the above parameters as well as the drop dynamics and surface flow experiments have been performed at constant temperature (20 ± 0.1 °C). All chemicals were of analytical purity and used without further purification.

Table 1

Composition and physical characteristics of the liquid/liquid systems of equal densities

System No.	Continuous Phase (L)			Drop Phase (L')		Surfactant Solution (S)	
	Composition (% vol)	μ (cP)	$\frac{\sigma_0}{L/L'}$ (dyn/cm)	Composition (% vol)	μ' (cP)	Composition (% vol)	$\frac{\sigma_1}{L/S}$ (dyn/cm)
1	Methanol 78 Water 22	1.33	10.2	Paraffin oil	80	Propanol 77.3 Water 22.7	3.5
2	NaNO ₃ 15.1 Water 84.9	1.10	28.2	Chlor benzene 50 Silicon oil 50	5.46	Benzylic alcohol 89 CCl ₄ 11	3.6
3	NaNO ₃ 14.9 Water 85.1	1.10	22.8	Chlor benzene 92 Silicon oil 8	1.03	Benzylic alcohol 89 CCl ₄ 11	3.6

Table 2

Surface tension gradient, Π , the ratio of the bulk viscosities, λ , the drop radius, a , and the values of the force $F_M(0)$ for the three systems given in Table 1

System No.	Π (dyn/cm)	λ	a (cm)	$F_M(0)$ (dyn)	Remarks
1	6.7 ± 0.3	60.15	1.19	0.82	The free drop remains practical nondeformable and the translational motion is insignificant (Fig. 5).
2	24.6 ± 0.3	4.96	0.46	11.92	The free drop might have slight or big deformations, but after 0.6–0.8 s, it returns to its initial form (Fig. 6). The translational motion (Fig. 6c) is evident from the initial position (Fig. 6a).
3	19.2 ± 0.3	0.94	0.46	28.57	The free drop, after 0.3–0.4 s, (Figs. 7a and 7b), breaks up into two droplets (Figs. 7c and 7d) which are also moving.

The mixtures making up the continuous L phase were placed in a thermostated parallelepipedic vessel of 1 dm³, made of transparent glass. The drop was made of various radii between 0.46 and 1.19 cm, using the mixtures described in Table 1. The L' liquid was carefully submerged by using a pipette into the continuous L aqueous phase and the density of the latter was then adjusted by adding small quantities of water or alcohol until the buoyancy of the drop practically disappeared.

After the system was stabilized, a small quantity (10^{-3} – 10^{-2} cm³) of the surfactant solution was injected with a micrometric syringe, in a point on the drop surface (injection point in Fig. 1). The injection was done either in a vertical direction (as in Fig. 5) or in different directions (Figs 6 and 7) and no influence of the mode of injection on the Marangoni flow or on drop movements and deformations were observed.

At the surfactant injection moment, the F_m is negative, acting on the opposite direction of the normal to the drop surface and having its effect the changing of the drop shape (Figs. 6a and 6b and Figs. 7a and 7b). For $\theta_f > \theta_0$ the resultant F_m becomes positive and its effect is the propulsion of the drop or the translational movement of the drop along the Oz axis (Figs. 6c, 7c and 7d).

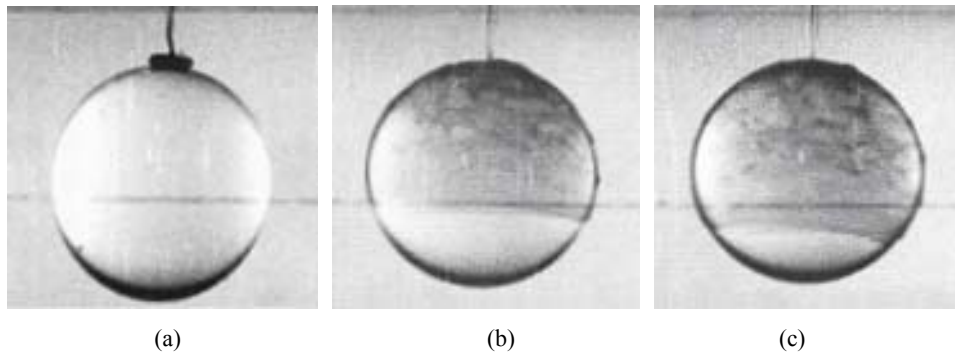


Fig. 5 – Filmed pictures of a nondeformable drop characterized by the system 1, $F_M(0) = 0.82$ dyn. The time of the surfactant front evolution: a) $t = 0$ s; b) $t = 1.02$ s; c) $t = 1.25$ s.

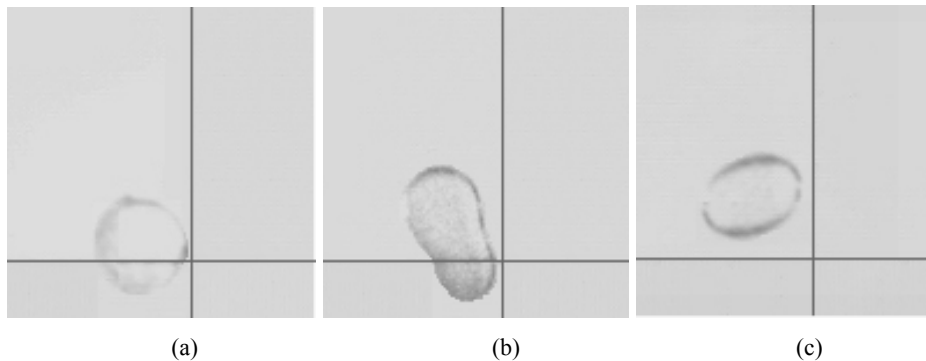


Fig. 6 – Filmed pictures of drop deformations characterized by the system 2, $F_M(0) = 11.92$ dyn. Time evolution of the drop: a) $t = 0$ (surfactant injection on drop surface); b) $t = 0.14$ s (deformation along Oz axis); c) $t = 0.44$ s (transversal deformation). Significant translation movement (c) from its initial position (a).

Under the surface tension gradients, the drop surface movement (Fig. 1) and the ventilation effect (Fig. 3) lead to the appearance of the Marangoni force, F_m ,

with its normal F_n and tangential F_t components (Fig. 4). In this investigation it is shown that the normal force component causes the drop deformations and it is the dominant force, for $\theta_f < \theta_0$, and it causes the hammer effect. The tangential force component provokes the displacement of the drop (such as lifting effect) and it is the major force for $\theta_f > \theta_0$.

The normal force acts like a hammer (hammer effect), deforming and even breaking up the drop. As shown by Eq. (18), the hammer effect appears directly proportional with Π and with the radius (a) of the drop and inversely proportional to λ . Therefore, at big values of λ ratio (Fig. 5, Table 2), the force is small and a significant deformation and the displacement of the drop, after the surfactant injection, are not observed. However, the normal force may produce some gentle surface waves, but these waves were not detectable in these experimental conditions.

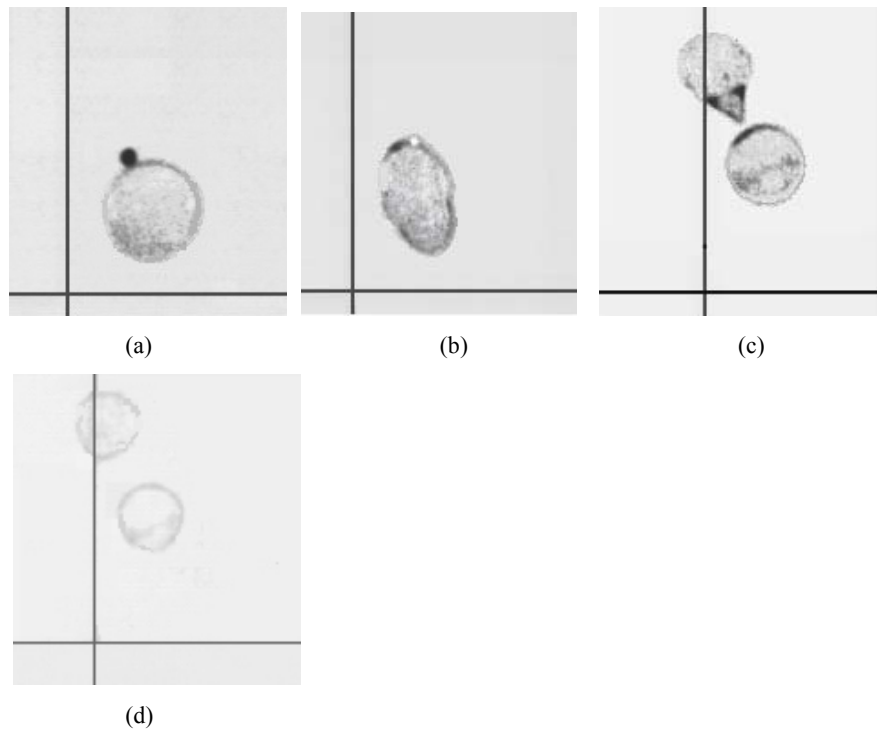


Fig. 7 – Filmed pictures of a breakup drop, characterized by the system 3. $F_M(0) = 28.57$ dyn. Time evolution of the drop: a) $t = 0$ s (surfactant injection on drop surface); b) $t = 0.12$ s (drop deformation); c) $t = 0.36$ s (break of the drop); d) $t = 0.43$ s.

At the surfactant injection moment the resultant Marangoni F_m force is negative, acting in the opposite direction of the normal to the drop surface. For intermediary (Figs. 6a and 6b) and small values of λ ratios (Figs. 7a and 7b), and for $\theta_f < \theta_0$, the

resultant Marangoni force F_m causes the visible modifications of the drop shape or even the break-up of the drop (Fig. 7c). For $\theta_f > \theta_0$ the resultant force F_m becomes positive and its effect is the propulsion of the drops or the translational movement of the drops along the Oz axis (Figs. 7c and 7d).

7. CONCLUSION

As shown above, the deformations of the drop under surfactants adsorption can not be attribute to a single mechanism, in our case a mechanical one, but we must consider also other factors, namely, the surface dilution and tip-stretching of the surface tension, as well as capillary forces. The results of our theoretical hydrodynamic model are in substantial agreement with the observed experimental data.

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