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## Specific properties of amphiphilic particles at fluid interfaces

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**Résumé.** — Nous présentons dans cet article une étude théorique et expérimentale de *particules amphiphiles* : il s'agit de sphères solides traitées de telle sorte qu'elles présentent une partie hydrophile et une partie hydrophobe. Ces grains ont un comportement spécifique à l'interface entre deux fluides de polarités différentes. En effet, dans une gamme étendue de valeurs du rapport entre les aires des surfaces hydrophile et hydrophobe, ils s'ancrent à l'interface le long de la frontière entre les deux parties. Outre l'intérêt intrinsèque lié à l'étude du mouillage de surfaces mixtes, ces particules amphiphiles pourraient avoir des applications industrielles notamment en ce qui concerne les procédés d'émulsification.

**Abstract.** — We present a theoretical and experimental study of *amphiphilic particles* : these are small solid spheres treated so that one part of the solid is hydrophilic whereas the other is hydrophobic. These beads have a specific behaviour at the interface between two fluids of different polarities since they are anchored at the interface along the border line between the two parts, in a large range of values for the ratio between the areas of the hydrophilic and hydrophobic sides. In addition to the intrinsic interest of the study of the wetting of mixed surfaces, these amphiphilic particles may be considered useful in technological processes such as emulsification.

### 1. Introduction.

The equilibrium position of solid particles at fluid interfaces is of considerable importance in a wide range of technological processes : flotation of ores, stabilization of emulsions, etc. Since the original study of von Reinders [1], much work has been devoted to the study of solid-liquid-liquid systems [2-8]. Most of these studies have been concerned with homogeneous solid particles. As for us, we have considered the case of heterogeneous particles. In previous articles [9-11], we have described the realization and the properties of objects that we call « Janus beads ». These objects are small glass spheres treated in such a way that one hemisphere is rendered hydrophobic whereas the other one remains hydrophilic. They may thus be considered as *amphiphilic solids* [12]. We have shown that Janus beads, in contrast with classical homogeneous spheres, exhibit the specific behaviour of anchoring at a fluid interface along their equatorial diameter i.e. at a fixed position independent of the different liquid-liquid and liquid-solid interfacial tensions involved. In the present article, we extend

the notion of Janus beads by considering the more general case of amphiphilic spheres, the surface of which is *nonsymmetrically* hydrophilic and hydrophobic. We first (part 2) present a theoretical discussion of the behaviour of such particles at a fluid interface when varying the asymmetry ratio which is, in a way, equivalent to the hydrophilic-hydrophobic balance (HLB) of surfactant molecules. We then describe the experimental methods used for preparation, characterisation and observation of these objects (part 3). Finally (part 4), the experimental results are compared with the theoretical predictions.

## 2. Janus model.

We present here a theoretical discussion for the equilibrium position of an amphiphilic bead at the interface between two fluids. In the following, W (like water) will denote the more polar fluid and O (like oil) the less polar one ; we refer to the hydrophilic part of the bead by P (for polar) and to the hydrophobic part by A (for apolar) ;  $\Delta$  represents the border line which separates A and P (cf. Fig. 1).

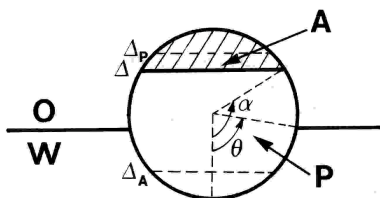


Fig. 1. — Schematic representation of an amphiphilic particle at a fluid-fluid interface. Polar and apolar liquids are denoted respectively by W and O. P and A refer to hydrophilic and hydrophobic parts of the bead respectively.

Let us recall briefly that, in the case of symmetric amphiphilic spheres (« Janus beads ») it has been shown [10] that the bead is — in its stable state — anchored along the border line  $\Delta$  no matter which two liquids are used, provided they satisfy the condition expressed by the double inequality :

$$\begin{aligned} \gamma(A, O) &< \gamma(A, W) \\ \gamma(P, W) &< \gamma(P, O) \end{aligned}$$

where  $\gamma(I, J)$  represents the interfacial tension between the two phases I and J. These conditions simply signify that the A hemisphere surface « prefers » the apolar (O) liquid while the P hemisphere « prefers » the polar (W) one. The equilibrium position of the bead is easily understood as the position which minimizes the solid-liquid interfacial energy as well as the liquid-liquid energy ; the latter contribution is all the more reduced as the interface is intercepted by the largest cross-section of the solid sphere.

For asymmetric amphiphilic beads, the situation is more delicate and we must consider the equilibrium conditions in terms of two angular parameters : the angle  $\alpha$  which characterizes the position of the  $\Delta$  line i.e. the asymmetry of the surface, and the angle  $\theta$  between the solid and the interface (Fig. 1). Two other relevant parameters are the contact angles  $\theta_A$  and  $\theta_P$  between, the A and the P surfaces respectively, and the two fluids.  $\theta_A$  and

$\theta_p$  correspond to the equilibrium angles given by the Young equation for homogeneous A and P solids :

$$\begin{aligned}\cos \theta_A &= \frac{\gamma(A, W) - \gamma(A, O)}{\gamma(O, W)} \\ \cos \theta_P &= \frac{\gamma(P, W) - \gamma(P, O)}{\gamma(O, W)}\end{aligned}$$

with  $\theta_A < \theta_P$  (in the case where the cosine is not defined, we take for the value of the corresponding angle, 0 or  $\pi$  depending on the sign of  $\gamma(\overset{A}{P}, W) - \gamma(\overset{A}{P}, O)$ ). Let  $\Delta_A$  and  $\Delta_P$  be the (fictitious) lines on the sphere, defined by  $\alpha = \theta_A$  and  $\alpha = \theta_P$  (Fig. 1).

For a given bead, the values of  $\theta_A$ ,  $\theta_P$  and  $\alpha$  are fixed by the preparation conditions and the equilibrium position  $\theta_e$  of the bead at the interface will be determined as the value of  $\theta$  which minimizes the total interfacial energy.

In the following, we discuss the case where the boundary line  $\Delta$  is parallel to the interface. We will see that this hypothesis is not very restrictive and permits us to obtain the general behaviour of the beads. In this case, the expression of the total surface energy  $E$  depends on the relative values of  $\theta$  and  $\alpha$  :

— if  $\theta \leq \alpha$

$$\begin{aligned}E(\theta) = E_P(\theta) &= 2 \pi R^2 [\gamma(A, O) (1 + \cos \alpha) + \gamma(P, O) (\cos \theta - \cos \alpha) + \\ &+ \gamma(P, W) (1 - \cos \theta) - \frac{1}{2} \gamma(O, W) \sin^2 \theta] \quad (1)\end{aligned}$$

— if  $\theta \geq \alpha$

$$\begin{aligned}E(\theta) = E_A(\theta) &= 2 \pi R^2 [\gamma(A, O) (1 + \cos \theta) + \gamma(A, W) (\cos \alpha - \cos \theta) + \\ &+ \gamma(P, W) (1 - \cos \alpha) - \frac{1}{2} \gamma(O, W) \sin^2 \theta]. \quad (2)\end{aligned}$$

The physical difference between the two expressions is the second term of the development corresponding to either a part of the polar surface immersed in oil in (1), or a part of the apolar surface immersed in water in (2). We note that the functions  $E_A$  and  $E_P$  considered separately (represented by the dotted line in Fig. 2) are minimized for  $\theta = \theta_A$  and  $\theta = \theta_P$  respectively.

Consequently, for amphiphilic beads, the energy minimum will depend on the relative position of  $\alpha$  compared with  $\theta_A$  and  $\theta_P$ . The three possible situations are summarized in figure 2 where the total energy is plotted as a function of  $\theta$ .

— If  $\alpha \in [\theta_A, \theta_P]$ , the energy is a minimum for  $\theta = \alpha$ . This corresponds to the « Janus behaviour » for which the anchoring is along the line  $\Delta$  which becomes a contact line between four phases (cf. Fig. 2b). Note that for  $\alpha = \frac{\pi}{2}$  (i.e. for a Janus bead) the condition  $\alpha \in [\theta_A, \theta_P]$  is equivalent to the double inequality mentioned previously. Besides, from a geometrical point of view, this condition is also equivalent to stating that the border line  $\Delta$  is comprised between  $\Delta_A$  and  $\Delta_P$ .

— On the other hand, if  $\alpha \notin [\theta_A, \theta_P]$  the energy is a minimum for either  $\theta_A$  or  $\theta_P$ . This implies that the bead has the same behaviour as a homogeneous apolar or polar bead (cf. Figs. 2a and 2c). In this case, the hypothesis that the border line  $\Delta$  is strictly parallel to the interface is not necessary : all the positions of the bead for which the angle between  $\Delta$  and the interface is smaller than  $\alpha - \theta_P$  (in the case of P-type behaviour), are energetically equivalent.

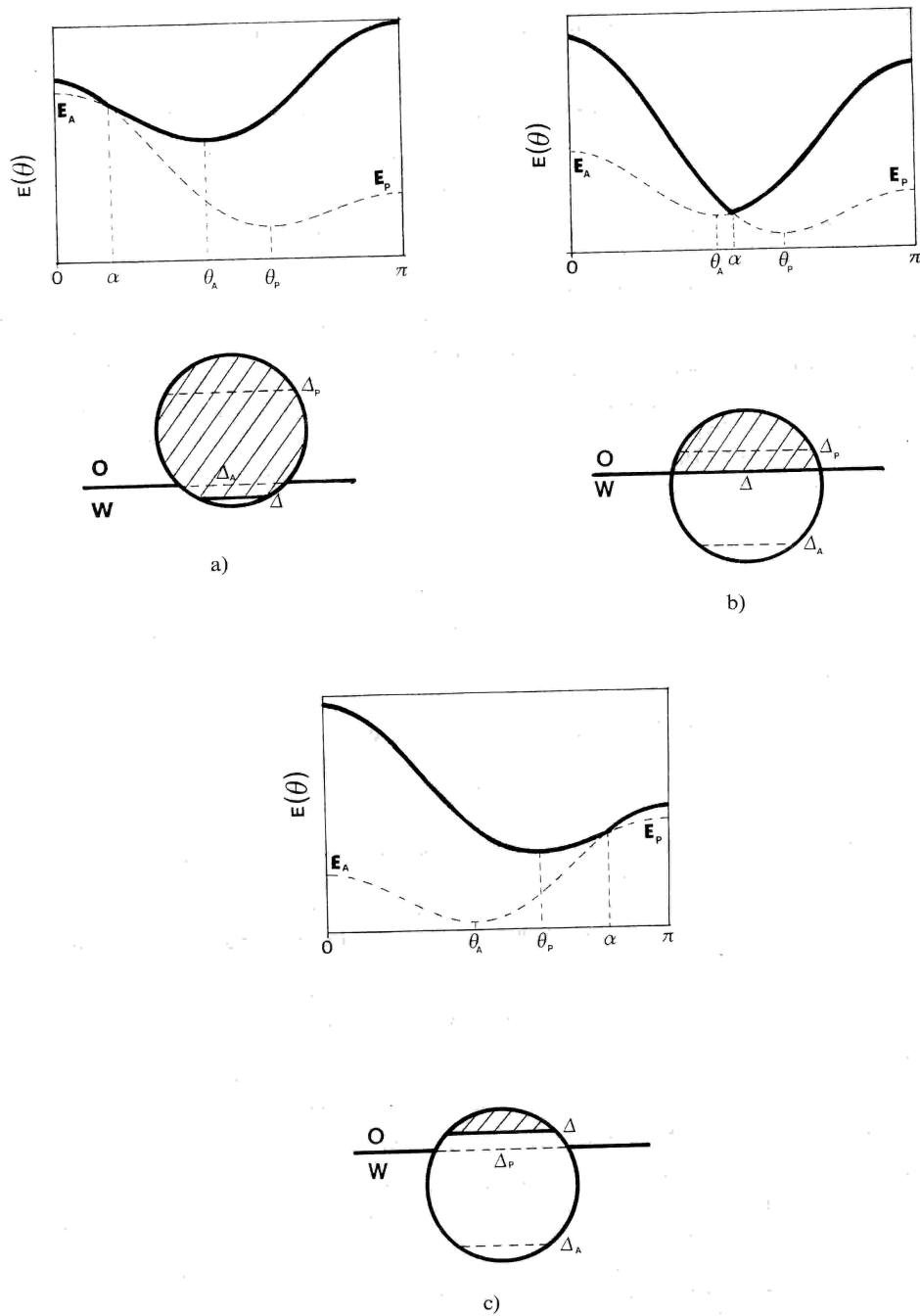


Fig. 2. — Variation of the total interfacial energy  $E$  as a function of  $\theta$  and schematic representation of the corresponding equilibrium position, for the three possible situations: (a)  $\alpha < \theta_A < \theta_P$ ; (b)  $\theta_A < \alpha < \theta_P$ ; (c)  $\theta_A < \theta_P < \alpha$ .

This model therefore predicts two possible regimes, one with J(Janus)-type and one with H(Homogeneous)-type behaviour. The change in regime could be observed either by varying  $\alpha$  (geometrical condition) at constant  $\theta_A$  and  $\theta_P$  or by varying  $\theta_A$  and  $\theta_P$  for a given bead (by changing the two liquids used). The results of the present calculation are similar to those obtained by the semi-quantitative discussion given in reference [10] in terms of canthotaxis angles. It is worth noting that the domain of  $\alpha$  for which the bead exhibits a J-behaviour is all the more extended as P or/and A solid surfaces have a great affinity for W or/and O liquids respectively. Under this condition, even a very asymmetric bead can undergo a Janus behaviour.

Similar calculations can be performed in the case of an amphiphilic bead trapped at the interface in the « wrong direction » i.e. with the A part oriented toward the W liquid. The expression for the energy is obtained by permuting in (1) and (2) the A and P indices and by replacing  $\alpha$  by  $\pi - \alpha$ . The analysis is straightforward and it can be shown that the bead always behaves as a homogeneous polar or apolar bead, obeying the Young equation. However, these situations lead to metastable positions as they always have higher energies than those corresponding to the « right direction » situations. In practice, small perturbations would enable the bead to flip-flop and return to stable equilibrium.

We emphasize that these calculations assume that gravity forces are negligible compared with capillary effects. The interface is then flat, undisturbed by the presence of the particles. One can show [13] that this approximation is valid in the limit of low Bond numbers which, in our experiments, are of the order of  $10^{-4}$ .

### 3. Preparation of amphiphilic solids and experimental methods.

3.1 PREPARATION OF THE BEADS. — The starting materials are commercial glass spheres which have been sifted in order to isolate the fraction of beads with a diameter of  $100 \pm 10 \mu\text{m}$ . The process used to obtain amphiphilic solids is described in detail in reference [9]. The basic idea is to protect partially the bead with a cellulose varnish (cf. Fig. 3)



Fig. 3. — Preparation of asymmetric amphiphilic beads.

and to render the free surface hydrophobic by chemical grafting of octadecyltrichlorosilane. The beads are then released by dissolving the varnish in acetone.

Symmetric or asymmetric amphiphilic beads can be obtained by varying the thickness  $e$  of the varnish layer. In the following, we shall characterize the beads by the value of  $e$ . For example, a «  $20 \mu\text{m}$  » bead of  $100 \mu\text{m}$  diameter is about  $\frac{1}{5}$  polar and  $\frac{4}{5}$  apolar. We have prepared several series of beads with  $e = 20, 40, 60,$  and  $80 \mu\text{m}$  giving samples which vary from quasi-apolar to quasi-polar spheres.

Homogeneous hydrophobic and hydrophilic beads are prepared under the same experimental conditions so that they can be used as reference objects.

3.2 VISUALIZATION OF THE BORDER LINE  $\Delta$ . — As described in the last paragraph, asymmetric amphiphilic beads may be easily obtained. In this case, the difficulty lies in the

characterization of these beads. Thus, for future experiments and interpretation, it is very important to determine with accuracy the position of the  $\Delta$  border line on the sphere, since the thickness  $e$  of varnish used during the preparation is simply a semi-quantitative indication. In the same way, the visualization based upon condensation patterns used in reference [9] is not precise enough in the present case. Thus, we were led to find a specific method which could determine precisely the position of the border line  $\Delta$  after the preparation.

The method which we used results from an observation due to C. Casagrande [14], on glass slides that had been partly treated : if a droplet is deposited on the border line between the polar and the apolar parts, it shifts spontaneously toward one of those two surfaces until it is anchored at the separation line, thus permitting us to specify it very precisely. The situation observed experimentally is schematized in figure 4 in the case of immersion oil which moves towards the polar part of the slide. This effect can be interpreted by considering the total interfacial energy for the solid-liquid-air system and has been studied theoretically by one of us [15] in a simpler geometry. This behaviour can be easily adapted to the case of beads, by covering them with an oil film which retracts from the apolar part. Beads are then observed and photographed under a microscope (Figs 5a and 5c). This method enables a precise characterization of any given bead by the determination of the angle  $\alpha$ .

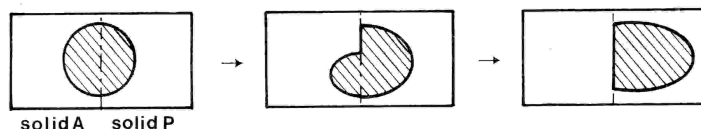


Fig. 4. — Evolution of a droplet deposited on the boundary between A and P solids.

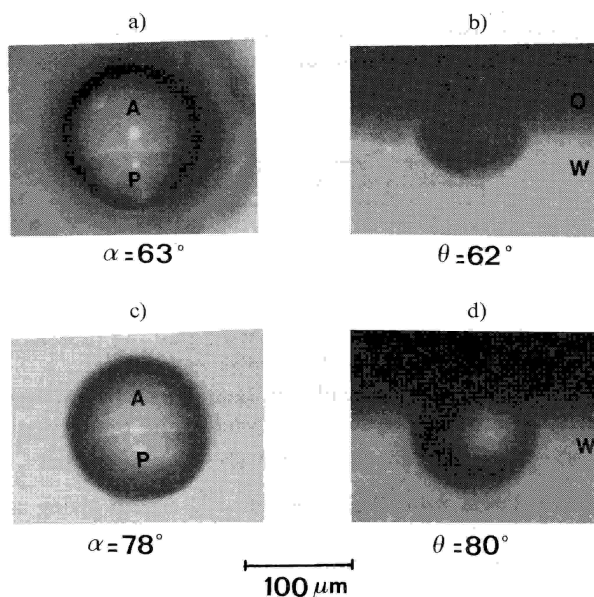


Fig. 5. — (a) (c) Visualisation of the border line  $\Delta$  in the case of « 20  $\mu\text{m}$  » and « 40  $\mu\text{m}$  » amphiphilic beads. (b) (d) Same beads trapped at the hexadecane-water interface.

**3.3 OBSERVATION OF THE BEADS AT A LIQUID-LIQUID INTERFACE.** — The bead is deposited at the air-water interface in a transparent cell with a square section  $1\text{ cm} \times 1\text{ cm}$  and then covered with oil. At the bead scale, meniscus effects due to the cell boundaries are negligible so that the interface can be considered flat. Horizontal observation is made by means of a binocular microscope. The microphotographs obtained (cf. Figs. 5b and 5d) are enlarged in order to determine with accuracy the angle  $\theta$  between the interface and the solid. Although it looks diffuse, the interface can be precisely located as the intersection of the sphere and its image in the water-oil diopter.

The uncertainty on the measurements of the two angles  $\alpha$  and  $\theta_e$  lies in the graphical determination of these angles on the photographs. In the two cases, the accuracy is estimated at  $5^\circ$ .

#### 4. Experimental results and discussion.

On the whole, we are able to determine the four physical quantities involved in the Janus model : the  $\alpha$  angle *via* the position of the  $\Delta$  line, the  $\theta_e$  angle at a given fluid interface and the Young angles  $\theta_A$  and  $\theta_P$  by using the homogeneous polar or apolar beads which have undergone the same surface treatment.

In order to test the validity of the Janus model, we have to check, first, that an asymmetric amphiphilic sphere is anchored along the line  $\Delta$  as long as  $\alpha \in [\theta_A, \theta_P]$  and, second, that one observes the change of regime from J to H-behaviour when varying the relative position of  $\alpha$  compared with  $\theta_A$  and  $\theta_P$ .

**4.1 VERIFICATION OF THE J-BEHAVIOUR FOR ASYMMETRICAL SPHERES.** — This experiment has been performed at the hexadecane-water interface for which we find :

$$\begin{aligned}\theta_A &= 43^\circ \pm 3^\circ \\ \theta_P &= 135^\circ \pm 3^\circ .\end{aligned}$$

These values are sufficiently different so that the  $\Delta_A$  and  $\Delta_P$  are close to the poles of the sphere. This permits us to vary the asymmetry of the bead in a large range while verifying the conditions required for the J-behaviour. This condition is *a priori* fulfilled for the four series of beads we have prepared.

Experimentally, we observe the position of all the samples at the interface, as described in part 3. It appears that the sphere position depends on the value of  $\alpha$  and, more quantitatively, that the measured contact angle  $\theta_e$  is always equal to  $\alpha$  (cf. Fig. 5). This demonstrates that the beads are anchored at the interface along the line  $\Delta$  and have, as defined above, a J-behaviour.

**4.2 THE CHANGE OF REGIME.** — In order to put into evidence an eventual change of regime, it is convenient to use two fluids for which large domains of  $\alpha$  lead to H and J-behaviours respectively. This is not easily obtained with oil and water for which, like in the hexadecane case,  $\Delta_A$  and  $\Delta_P$  are close to the poles. However, this condition can be realized at the air-water interface due to the values of the contact angles  $\theta_A$  and  $\theta_P$  (see Tab. I). In this case, approximately one half of the sphere corresponds to  $\alpha \in [\theta_A, \theta_P]$  and the other half to  $\alpha \notin [\theta_A, \theta_P]$  (cf. Fig. 6a).

The experimental procedure is the following : each bead is first observed and photographed at the air-water interface. For comparison, hexadecane is then poured onto the water so that the same bead is trapped at the hexadecane-water interface. These experiments have been performed on numerous beads of each series and lead to similar conclusions illustrated by the

Table I. — Values of the equilibrium angle  $\theta_e$  of different beads at air-water and hexadecane-water interfaces.

Interface \ Bead	Apolar	Polar	Amphiphilic			
			20 $\mu\text{m}$ $\alpha = 63^\circ$	40 $\mu\text{m}$ $\alpha = 78^\circ$	60 $\mu\text{m}$ $\alpha = 110^\circ$	80 $\mu\text{m}$ $\alpha = 132^\circ$
$\frac{\text{Hexadecane}}{\text{Water}}$	43°	135°	62°	80°	109°	132°
$\frac{\text{Air}}{\text{Water}}$	88°	145°	85°	88°	110°	132°

examples given in figure 6b and summarized in table I. The change of regime is observed at the air-water interface between the samples « 40  $\mu\text{m}$  » and « 60  $\mu\text{m}$  ». In the case of beads with  $e \leq 40 \mu\text{m}$  the contact angle remains constant obeying the Young condition and the amphiphilic solid has the same behaviour as a homogeneous apolar bead. For comparison, at the hexadecane-water interface the same beads are anchored along  $\Delta$  (J-behaviour) according to the preceding paragraph.

In the case of beads with  $e \geq 60 \mu\text{m}$ , we observe, as expected, the same J-behaviour at both interfaces.

### 5. Conclusion.

In conclusion, we have observed that, in agreement with our theoretical predictions, two different regimes are obtained for the anchoring of amphiphilic solids at a free interface : one regime that we called J-type, where the particle is anchored along the border line which thus appears as a contact line between four phases ; in the other regime, the bead behaves like a homogeneous one obeying the Young equation. It is important to emphasize that, if the difference of polarity between the two fluids is significant, the J-behaviour dominates in a large range of geometrical surface asymmetries.

These theoretical and experimental results may be of some importance in technological processes where such particles could be exploited for their surfactant properties. On the one hand, it has been shown that it is sufficient for a small fraction of the surface to be treated to induce the anchoring at the interface. On the other hand, it should be possible, by analogy with the Bancroft rule [16], to obtain different types (direct or inverse) of dispersed systems by varying the asymmetry ratio.

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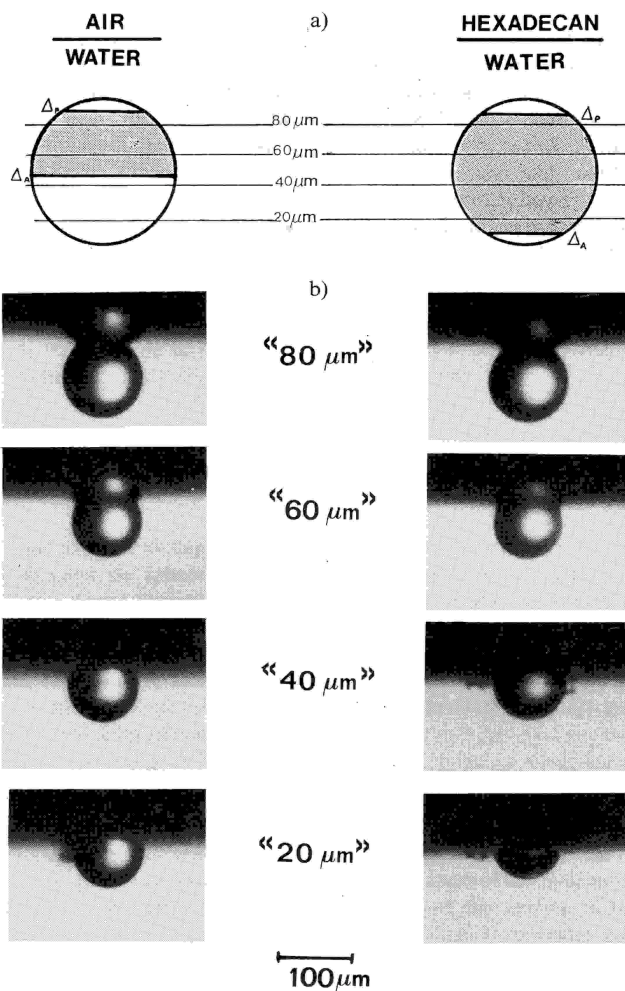


Fig. 6. — (a) Schematic representation of the domain in which the beads have a J behaviour (dark zone) in the cases of air-water and hexadecane-water interfaces. (b) Comparison of the equilibrium positions of « 20  $\mu\text{m}$  », « 40  $\mu\text{m}$  », « 60  $\mu\text{m}$  », « 80  $\mu\text{m}$  » amphiphilic beads at air-water and hexadecane-water interfaces.

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