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Deviations from the spontaneous curvature in surfactant films : effects on the second virial coefficient and interfacial properties of the microemulsions

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Résumé. — On évalue les contributions de l'énergie de courbure du film interfacial de tensioactifs aux interactions attractives entre gouttelettes dans les microémulsions diluées d'une part, et aux tensions interfaciales des systèmes triphasiques de Winsor loin des points critiques d'autre part. (1) Dans une microémulsion diluée d'eau dans l'huile où la courbure des gouttelettes d'eau (définie comme positive) est légèrement plus grande que la courbure spontanée C_0 du film interfacial, une fluctuation possible à l'équilibre thermodynamique est l'union de deux gouttelettes en un dimère de faible énergie de courbure. Ce processus donne une contribution attractive au second coefficient du viriel entre gouttelettes en bon accord avec certaines observations expérimentales. (2) L'interface entre une microémulsion et une phase en excès, de l'huile par exemple, est soit *fermée* par un film plan de tensioactifs de type Langmuir, dans ce cas un film mouillant d'eau sépare le film et la microémulsion, soit *ouverte*, i.e. traversée par des pores d'huile. La courbure du film de tensioactifs de la microémulsion dans la région interfaciale est en moyenne dirigée vers l'huile dans le premier cas et vers l'eau dans le second cas. Nous montrons à l'aide du modèle de microémulsions aléatoires proposé par de Gennes, que, dans les systèmes triphasiques de Winsor, l'interface eau/microémulsion passe du cas « ouvert » au cas « fermé » et l'interface huile/microémulsion du cas « fermé » au cas « ouvert », quand la salinité de l'eau, i.e. C_0 , augmente. Cette évolution est en accord avec des expériences d'ellipsométrie. Quand $|C_0|$ est petit, les deux interfaces sont « ouvertes » et la différence entre les tensions de surface des deux interfaces est proportionnelle à C_0 . On retrouve qu'à la salinité optimale ($C_0 = 0$), cette différence est nulle.

Abstract. — One evaluates the contributions of the surfactant interfacial film bending energy first to the attractive interactions between droplets in dilute microemulsions and second to the interfacial tensions in triphasic Winsor systems far from the critical points. (1) In a dilute water in oil microemulsion where the water droplet curvature (defined as positive) is slightly larger than the interfacial film's spontaneous curvature C_0 , a possible fluctuation at thermodynamic equilibrium is the fusion of two droplets in a dimer of low curvature energy. This process gives an attractive

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contribution to the droplet second virial coefficient which is in good agreement with certain experimental observations. (2) The interface between a microemulsion and an excess phase, oil for example, is either *closed* by a flat Langmuir type surfactant film, in which case a wetting water layer separates the film and the microemulsion, or *open*, i.e. traversed by oil pores. The microemulsion surfactant film curvature is on average directed towards oil in the first case and towards water in the second case. We show by using the microemulsion random structure model proposed by de Gennes that, in the Winsor triphasic systems, the water/microemulsion interface evolves from the case « open » to the case « closed » and the oil/microemulsion from the case « closed » to the case « open », when the water salinity, i.e. C_0 , increases. When $|C_0|$ is small, the two interfaces are « open » and the difference between the surface tensions of the two interfaces is proportional to C_0 . One recovers the result that this difference vanishes at the optimal salinity ($C_0 = 0$).

1. Introduction.

Recently many features of microemulsion structure and phase behaviour have been interpreted by considering the curvature energy of the surfactant interfacial film between oil and water, which becomes important because the film surface tension is almost zero [1-3].

The curvature energy per unit area is written :

$$E = \frac{1}{2} K (C^2 - 2 C_0 C). \quad (1)$$

C is the local interface mean curvature, $C = 1/R_1 + 1/R_2$, where R_1 and R_2 are the principal radii of curvature. By convention, a flat interface ($C = 0$) has a zero curvature energy and the curvature is positive for water in oil droplets.

The first term describes the flexibility of the interfacial film ; K is a rigidity constant (in microemulsions, $K \sim 10^{-14}$ erg) [4] ; if K is larger than kT , the oil, water and surfactant are ordered in birefringent lamellar phases [1, 4], if K is smaller, disordered microemulsions may be formed.

C_0 is the spontaneous film curvature. C_0 depends on the geometry of the surfactant and cosurfactant molecules [5] and on their interactions with oil and water ; it is related to the Winsor « R -ratio » [6] and to the surfactant Hydrophile-Lipophile-Balance [7], but has never been measured quantitatively because, in general, the surfactant film structure in lyotropic liquid crystals and microemulsions is not only imposed by the curvature energy, but also by long range van der Waals and electrostatic forces, steric interactions and dispersion entropy ; thus the local film curvature differs in general from C_0 . In the two situations discussed below, this deviation leads to remarkable effects :

i) in dilute droplet microemulsions, structural rearrangements which lower the film bending energy may be the origin of apparent attractive interactions between droplets ;

ii) in Winsor III microemulsions [6-9], the curvature energy contributions to the interfacial tensions between the oil phase and the microemulsion middle phase and between the microemulsion and the water phase may explain the interface structure changes and the interfacial tension variations observed as the water salinity varies.

2. Spontaneous curvature and attractive interactions in dilute microemulsions.

Attractive interactions between dilute spherical water droplets have been observed in many water in oil microemulsions [10-13]. They are too large to be only due to pure van der Waals interactions between the droplet water cores separated by the interfacial film. To describe them, Lemaire, Bothorel and Roux [14] assume that the spherical surfactant (and cosurfactant) layers of two interacting droplets interpenetrate ; the resulting increase in van der Waals interactions satisfactorily describes the experimental second virial coefficient [13, 15]. However, in many cases,

particularly in salt free microemulsions with ionic surfactant and alcohol, the interpenetration effects could be in concurrence with the curvature effects for two reasons :

i) ionic surfactants like S.D.S. (sodium dodecylsulfate) are very hydrophilic. S.D.S. forms oil in water micelles ; the spontaneous curvature C_0 of a pure S.D.S. film should be very negative ; even if alcohol addition in the film increases C_0 , it may happen that C_0 remains slightly negative, while the actual droplet curvature is positive ;

ii) the addition of salt to water diminishes the attractive interactions between neutral water in oil droplets [11, 12]. This effect is not explained by the interpenetration mechanism.

The idea that curvature effects can lead to apparent attractive interactions arises from the work of Safran [16], who has shown that a spherical droplet microemulsion is unstable with respect to shape fluctuations which lower the surfactant bending energy at small $C_0 R$ values (R , droplet radius). Here, to evaluate the strength of these effects, we specify one way by which the Safran instability begins and use a perturbation approach. We do not take into account all the possible water and surfactant arrangements, but consider only the formation of droplet dimers which is the main process contributing to the apparent second virial coefficient of the droplets.

In the non-perturbed state, the water in oil microemulsion (ϕ_w , water volume fraction, c_s , surfactant concentration) is made of monodisperse hard spheres, each sphere has a radius R ($R = 3 \phi_w / c_s \Sigma$, Σ , area per surfactant polar head), volume V_1 , area S_1 and an internal curvature energy E_1 ($E_1 = 8 \pi K(1 - C_0 R)$). If the surfactant film is incompressible and is curvature independent, the total film area and surface energy are constant, and the initial state is perturbed by the dimer formation in two main ways :

i) because the total water volume and film area are conserved, a dimer made of two spherical droplets cannot be spherical, but has a surface with regions of high and low (possibly negative) curvature (Fig. 1) ; in the favourable cases ($C_0 R \ll 1$), the curvature energy will be lowered ;

ii) the translational entropy is decreased.

To study these effects, we proceed as follows. In order to separate the microemulsion free energy into two terms, the translation entropy and the curvature energy, we neglect the small entropy associated to the dimer shape fluctuations. This amounts to approximating the dimer free energy by its curvature energy, which has to be minimized at constant volume and area. As this minimization is not possible analytically, we reduce the variational problem by considering a very small class of dimer shape. Then, assuming that all the dimers have the same minimal shape and curvature energy, we derive the microemulsion equation of state.

Fig. 1. — Two identical spherical droplets (thin line) coalesce to form a dimer (thick line). The total volume and area are conserved. This example is calculated with the $m = 0$, $l = 2$ spherical harmonic.

2.1 DIMER SHAPE AND CURVATURE ENERGY. — The problem of minimizing the curvature energy of a deformable globule at constant volume and area has been studied numerically by Helfrich [17]. Applied to our case, his results show that, for $C_0 R \ll 0$, a dimer adopts an oblate biconcave discoid shape rather than a prolate dumbbell like shape, whereas for $C_0 R \simeq 0$, it probably prefers an elongated prolate shape. We have used these indications to obtain two simple shapes (biconcave or convex), which allows an estimation to be made of an upper bound of the dimer curvature energy and the free energy in both cases : $C_0 R \ll 0$ and $C_0 R \simeq 0$. (In these estimates, we neglect possible cosurfactant segregation as a function of film curvature, C_0 and K are assumed to be curvature independent).

2.1.1 Biconcave shape. — We describe the dimer shape by a development in spherical harmonics limited to the quadrupolar terms and calculate its curvature energy by neglecting anharmonic terms (cf. Ref. [16] and note). In spherical coordinates, the dimer surface equation is :

$$r(\theta, \phi) = \rho \left(1 + \sum_{m=-2}^{m=2} a_{2,m} Y_2^m(\theta, \phi) \right), \quad (a_{2,m}^* = (-1)^m a_{2,-m}).$$

To the first order in A , defined by $4 \pi A = \sum_{m=-2}^{m=2} |a_{2,m}|^2$, the dimer volume V_2 , surface S_2 and curvature energy $E_2^{\text{b.s.}}$ are :

$$V_2 = (8 \pi / 3) R^3 = (4 \pi / 3) \rho^3 (1 + 3 A) \quad (2)$$

$$S_2 = (8 \pi) R^2 = (4 \pi) \rho^2 (1 + 4 A) \quad (3)$$

$$E_2^{\text{b.s.}} = (8 \pi) K ((1 - C_0 \rho) + 6 A (1 - C_0 \rho / 2)). \quad (4)$$

Equations (2) and (3) determine, A and $E_2^{\text{b.s.}}$ uniquely :

$$\rho = 1.107 R; \quad A = 0.154$$

$$E_2^{\text{b.s.}} = 16 \pi K (0.96 - 0.81 C_0 R).$$

2.1.2 Convex prolate shape. — The simple shape of this kind allows an exact calculation of the curvature energy in a spherocylinder (cylinder length L , radius ρ_c) to be made. The constraints of volume and area conservation impose :

$$L = 4 R = 2(1 + \sqrt{3}) \rho_c$$

$$E_2^c = 16 \pi K ((5 + \sqrt{3})/8 - (\sqrt{3}/2) C_0 R) = 16 \pi K (0.84 - 0.87 C_0 R).$$

By comparing $E_2^{\text{b.s.}}$ and E_2^c with $2 E_1$, the curvature energy of two separated droplets, one deduces that the dimer formation is energetically favourable as soon as $C_0 R < 1.2$. Assuming that one may compare the approximate calculation of $E_2^{\text{b.s.}}$ with the exact calculation of E_2^c , one recovers Helfrich's results ; for $-2 < C_0 R < 1.2$, a dimer has a prolate spherocylindrical shape, the energy gain is mainly due to the flexibility term ; for $C_0 R < -2$, the dimer has a biconcave shape, the energy gain is mainly due to the spontaneous curvature term ; note that, in the harmonic approximation used in this case, a prolate shape has the same energy as an oblate shape.

The energy difference $2 E_1 - E_2$ is :

$$2 E_1 - E_2 = \alpha K (1 - \beta C_0 R).$$

If $C_0 R > -2$, $\alpha = 8$, $\beta = 0.85$; if $C_0 R < -2$, $\alpha = 1.91$, $\beta = 5$.

2.2 EFFECTIVE DROPLET SECOND VIRIAL COEFFICIENT. — With our simplifying assumptions, we can use Tanford's procedure [18] to evaluate the apparent droplet virial coefficient. If one describes the dimer formation by a single chemical equilibrium ($X + X \rightleftharpoons X_2$), the equilibrium constant is :

$$Z = \exp(-(2E_1 - E_2)/kT) = \phi_1^2/\phi_2$$

ϕ_1, ϕ_2 are the monomer and dimer volume fractions, to second order in ϕ_w :

$$\phi_2 = \phi_w^2/Z \quad \text{and} \quad \phi_1 = \phi_w - \phi_w^2/Z.$$

The dimer formation reduces the osmotic pressure Π by the quantity :

$$\Delta\Pi = (kT/2 Z V_1) \phi_w^2.$$

The dimer contribution B_a to the second virial coefficient B defined by :

$$\Pi/kT = (\phi_w/V_1)(1 + B\phi_w/2)$$

is :

$$B_a = -(1/Z).$$

By including the hard-sphere contribution $B_{H.S.} = 8$ (one neglects the difference between the hard sphere radius and the water core radius), the total second virial coefficient is :

$$B = 8 - \exp((\alpha K/kT)(1 - \beta C_0 R)). \quad (5)$$

This equation has two consequences for water in oil microemulsions :

- i) when the droplet radius is kept constant, B increases as C_0 increases, i.e. the droplets harden as the interfacial film becomes more lipophilic (e.g. if one uses surfactant or alcohol molecules with a longer aliphatic tail) or less hydrophilic (e.g. salt is added to water);
- ii) at constant K and C_0 , B decreases as the droplet radius increases if C_0 is negative.

2.3 COMPARISON WITH EXPERIMENT. — The theory presented here predicts that dimers associated to the attractive interactions in very dilute droplet microemulsions always exist, this is indeed verified in recent electric birefringence experiments [19].

Equation (5) may interpret the yet unexplained droplet hardening caused by salt addition to water in oil microemulsions ; it also predicts the observed evolution when one varies the alcohol chain length or droplet radius. In this last respect, it may however be difficult to separate the present model from the Lemaire model, because both predict the same observed trends. As an example, we have analysed the data of reference [13]. In the S.D.S.-hexanol-dodecane-water system studied, the alcohol to surfactant ratio in the film remains approximately constant as the droplet radius R is increased, thus we suppose that K and C_0 are constant. Equation (5) fits correctly the data with α and β constant and gives :

$$\alpha K/kT = 1.15 \quad \beta C_0 = -1.9 \times 10^{-2} \text{ \AA}^{-1}.$$

Such hypothetical estimates should be correlated with microemulsion phase behaviour. In the S.D.S.-pentanol-cyclohexane-water system of reference [11], where dimers have been evidenced by neutron scattering, one observes that B does not depend on the droplet radius and that these microemulsions are adjacent to lamellar phases in the phase diagram [4]. Both observations suggest that C_0 is practically zero.

3. Spontaneous curvature and Winsor III phases interfacial tensions.

Because of the potential applications of Winsor III systems to tertiary oil recovery [31], the very low interfacial tensions $\gamma_{m/o}$ and $\gamma_{m/w}$ between the microemulsion (m), the upper oil phase (o) and lower brine phase (w) have been much studied [20]. However their relations with the middle-phase

structure, which is now reasonably well described theoretically [21-23] and experimentally [24, 25], are yet unclear. In particular, the local structure of the o/m and w/m interfacial regions is little known. Surface tensions [26] and ellipsometry measurements [27] have evidenced two extreme cases :

- i) the case of a thick diffuse critical interface associated with a very small interfacial tension ($\sim 10^{-5}$ dyne/cm) ;
- ii) the case of a narrow interface associated with a relatively large interfacial tension ($\sim 10^{-2}$ dyne/cm). In this case, an ellipsometry experiment [27] has shown that a Langmuir film probably separates the microemulsion from either the oil phase or the water phase and that a thin wetting layer of the third phase exists between the Langmuir film and the microemulsion.

As salinity increases from the lower salinity level where the water phase appears to the upper salinity level where the oil phase disappears, the m/w interface moves from case (i) to case (ii) and the o/m interface from case (ii) to case (i). In the medium salinity range, the interface structure is unknown.

Up to now, no unified theory of the microemulsion interfacial tensions and interfacial structure exists. The recent structure models [21-23], which describe the middle-phase as a random dispersion of oil and water in cells of size ξ , the surfactant being at the oil-water interface, have been only applied to the case of a *diffuse* interface, this characteristic arising either from the randomness of the microemulsion or from the vicinity of a critical point.

Talmon and Prager have shown that their structure model, which neglects curvature effects, naturally leads to a diffuse microemulsion interface of thickness ξ . The interfacial tension, calculated in a van der Waals theory [28], has an entropic origin and is small because ξ is large ($\gamma \sim T/\xi^2$, $\xi \sim 100$ Å).

More recently, by using a model which includes the curvature energy of the surfactant film and by treating the dispersion scale ξ as a variational parameter, Widom [23] has interpreted the Winsor microemulsion phase behaviour and has pointed out the special nature of the Winsor critical points, which would be tricritical ; he then has discussed the microemulsion interfacial tensions within the frame of critical phenomena theory [29].

Here, by using also the random structure models and neglecting van der Waals interactions, whose contributions to the microemulsion interfacial tensions have been calculated by Chun Huh [30], we study the narrow non-critical middle-phase interfaces. We focus the (mainly qualitative) discussion on curvature effects and demonstrate a mechanism which interprets the appearance of a Langmuir film at a microemulsion interface.

3.1 « OPEN » versus « CLOSED » INTERFACES (Fig. 2a-c). — When a classical microemulsion made of water in oil droplets in a continuous oil phase coexists with a water phase in excess, there is a Langmuir flat surfactant film at the water/microemulsion interface, the interface is « closed ».

Fig. 2. — Three possible structures of a microemulsion middle-phase/oil phase interface. Progression from and open to a closed interface as the spontaneous curvature decreases and changes its sign. (a) and (b) : the m/o interface is open, if $C_0 > 0$, the surfactant film is preferentially bent towards water. (c) : the m/o interface is closed by a flat Langmuir film and a water wetting layer ; if $C_0 < 0$, the microemulsion surfactant film is preferentially bent towards oil.

However, if the same microemulsion coexists with a pure oil phase, the microemulsion/oil interface is the analog of a liquid vapour interface and there is no Langmuir film ; the interface is then « open ».

Inside the middle phase, the interfacial film curvature fluctuates so strongly that the oil and the water are randomly dispersed in microscopic domains. At first sight, it seems that the microscopic interface between oil and water defined by the surfactant film in the w/m or o/m interfacial region cannot be flat. At the m/o interface for example, there should be continuous (but fluctuating) path going through the oil from the upper phase into the middle phase. This implies that the interfacial film should be on average bent towards water. In this case, we say that the m/o interface is « open » to oil (Fig. 2a). Similarly the w/m interface might be « open » to water, with the interfacial film bent on average towards oil.

If the two w/m and o/m interfaces are « open » and if the film's spontaneous curvature is not zero, the curvature energy E_c of the soap film in each interface is different. If C_0 is positive, $E_c(w/m)$ is larger than $E_c(o/m)$ and one can then imagine geometrical rearrangements of the w/m interface which lower its spontaneous curvature energy (Fig. 2b, c).

The experiments suggest an extreme case : one can transform the high energy w/m interface into a low energy o/m interface by introducing a wetting oil layer between the microemulsion and water (Fig. 2c). Then one needs a Langmuir flat surfactant film on the new oil-water interface. In this case, we speak of a « closed » interface.

Finally, starting from the « closed » w/m interface, one can generate all the possible different structures of a w/m interface by creating water pores through the oil wetting layer. Here we will study only the two extreme cases :

- i) the randomly open interface
- ii) the completely closed interface.

3.2 SURFACE ENERGY OF A RANDOMLY OPEN INTERFACE. — In the de Gennes or Widom model, the oil and the water (in volume fraction ϕ_o and ϕ_w) are distributed randomly with probability ϕ_o and ϕ_w in cubes of size ξ , the surfactant being at the oil/water interface. ξ is the persistence length of the surfactant film ; as the probability to find a cube facet occupied by surfactant is $\phi_o \phi_w$, one has :

$$\xi = 6 \phi_o \phi_w / c_s. \quad (6)$$

Far from a critical point, the o/m and w/m interfacial regions have a thickness of order ξ , so we restrict each of them to only one cube layer. Our main assumptions are the following : ξ is not a variational parameter [23] and does not change in the interfacial regions ; the interfaces are randomly open, this means that the oil and the water remain randomly distributed in the interfacial cubes with the same probability as in the bulk (Fig. 3).

Fig. 3. — The randomly open interface in the cube model. Only the interfacial layer is represented. The water is shaded, $\phi_w = 0.35$.

There are two contributions to the surface tensions. One comes from the entropy, the other from the curvature energy.

The entropic contribution has been evaluated by Talmon and Prager [28], its order of magnitude is :

$$\gamma^e = kT/\xi^2. \quad (7)$$

Note that this contribution is the same for both w/m and o/m interfaces. The surface tension difference between the two interfaces will only be due to the curvature energy.

In the cube model, the curvature is concentrated on the cube edges. For a given edge, the curvature energy ε_c may take three values :

- i) $\varepsilon_c = 0$, if there is no soap on the edge or if the film is flat.
- ii) $\varepsilon_c = \lambda K(1 - \mu C_0 \xi)$, (λ and μ positive constants of order of 1), if the film is bent towards water at the edge.
- iii) $\varepsilon_c = \lambda K(1 + \mu C_0 \xi)$, if the film is bent towards oil.

At the m/o interface, only edges located on the upper plane of the interfacial region contribute to the curvature energy excess with respect to the bulk, their curvature energy can only take the values 0 or $\lambda K(1 - \mu C_0 \xi)$. As the number of such edges where the film is bent towards water is on average $4 \phi_o \phi_w$ per square of area ξ^2 , the curvature energy contribution to the o/m interfacial tension is :

$$\Gamma_{m/o}^c = (4 \phi_o \phi_w \lambda K(1 - \mu C_0 \xi) - 2 \varepsilon_c^b)/\xi^2$$

ε_c^b is the mean curvature energy per cube edge in the bulk and is a function of K , C_0 , ξ , ϕ_o and ϕ_w . It has been discussed by de Gennes from symmetry arguments [22], it could also be evaluated by counting and weighting the ways of filling with oil and water a cube of size 2ξ containing 8 subunits of size ξ ; then one describes all the possible film configurations around a cube corner; one has :

$$\varepsilon_c^b = \alpha_1 K \phi_o \phi_w (1 - \alpha_2 \phi_o \phi_w + \mathcal{O}((\phi_o \phi_w)^2)) - \alpha_3 C_0 \xi \phi_o \phi_w ((\phi_o - \phi_w) + \mathcal{O}(\phi_o^3 - \phi_w^3))$$

where α_1 , α_2 and α_3 are positive constant of order 1.

Finally, the total o/m interfacial tension is within this model :

$$\gamma_{m/o}^1 = \gamma^e + (4 \phi_o \phi_w \lambda K(1 - \mu C_0 \xi) - 2 \varepsilon_c^b)/\xi^2. \quad (8)$$

Similarly, the w/m interfacial tension is :

$$\gamma_{m/w}^1 = \gamma^e + (4 \phi_o \phi_w \lambda K(1 + \mu C_0 \xi) - 2 \varepsilon_c^b)/\xi^2. \quad (9)$$

We turn now to the case of a closed interface to establish the corresponding equations.

3.3 SURFACE ENERGY OF A CLOSED INTERFACE. — We use a very crude model where, say, the m/o macroscopic closed interface is a superposition of a randomly open w/m interface, a water wetting layer and a Langmuir flat surfactant film. We forget the possible existence of oil pores through the water wetting layer, we only remember that this possibility requires the wetting layer thickness to be of order ξ .

Then, the oil-microemulsion surface tension $\gamma_{m/o}^2$ is the sum of :

- i) $\gamma_{m/w}^1$, the surface tension of the randomly open interface calculated in section 3.2;
- ii) the free energy of the wetting layer, $\gamma_{w.1}$. If one neglects van der Waals interactions, one only has to consider the entropy loss due to the localization of the water at the microemulsion interface. As the wetting layer thickness is of order ξ , $\gamma_{w.1} \sim kT/\xi^2$.
- iii) the Langmuir film free energy, γ_f . The microemulsion stability imposes that γ_f is very small, also of order kT/ξ^2 [1, 22].

We regroup the two last contributions in a phenomenological parameter γ^* (of order kT/ξ^2), finally :

$$\gamma_{m/o}^2 = \gamma_{m/w}^1 + \gamma^* . \quad (10)$$

Similarly, one would have for a m/w closed interface :

$$\gamma_{m/w}^2 = \gamma_{m/o}^1 + \gamma^* . \quad (11)$$

3.4 DISCUSSION. — We first note from equations (8) to (11) that the o/m and w/m interfaces cannot be closed at the same time. If one limits the discussion to our two extreme cases, there are three different situations depending on the value of the spontaneous curvature with respect to the parameter C_0^* , which is a characteristic curvature of order ξ^{-1} :

$$C_0^* = 2 \gamma^* \xi / \lambda \mu K \phi_o \phi_w$$

- i) if $C_0 < -C_0^*$, the middle phase will minimize its surface free energy with an open w/m interface and a closed m/o interface;
- ii) if $-C_0^* < C_0 < +C_0^*$, the two interfaces are open;
- iii) if $C_0 > C_0^*$, the w/m interface is closed while the m/o interface is open.

Experimentally, one increases the spontaneous curvature of an ionic surfactant film by increasing the water salinity, one then sees that the sequence (i), (ii), (iii) corresponds to the sequence observed in the ellipsometry experiments [27]. The case (ii), which corresponds to a small spontaneous curvature and a middle range salinity is particularly interesting. Then, the difference $\Delta\gamma$ between $\gamma_{m/o}$ and $\gamma_{m/w}$ is directly related to the spontaneous curvature and might be used to estimate its order of magnitude :

$$\Delta\gamma = -8 \lambda \mu K C_0 \phi_o \phi_w / \xi = - (4/3) \lambda \mu K C_0 c_s \Sigma . \quad (12)$$

Taking $K \sim 10^{-14}$ erg [4], $1/C_0 \sim 100 \text{ \AA}$ and $1/c_s \Sigma \sim 100 \text{ \AA}$, one estimates $\Delta\gamma \sim 10^{-2}$ dyne/cm, which is the right order of magnitude.

Note that if $C_0 = 0$, one expects that the middle phase contains as much oil as water [23] and that $\Delta\gamma = 0$. This is indeed what is observed in many Winsor systems at the optimal salinity [31].

4. General conclusions.

We have shown on simple models that the recent ideas describing microemulsion structure and phase behaviour as resulting from a competition between the oil and water dispersion entropy and the surfactant film surface and curvature energies could in certain cases explain the observed values of :

- i) the virial coefficients of interacting droplets in dilute microemulsions;
- ii) the surface tensions of non-critical Winsor III systems.

By measuring these two quantities, one can obtain direct information on the curvature elasticity parameters of the surfactant interfacial film. Hopefully, it will be possible to correlate both measurements.

We have also interpreted the existence of open or closed microemulsions interfaces. It would be interesting to get information on the transition between the two types of interfaces as the film's spontaneous curvature changes, and to extend the discussion to the case of critical interfaces.

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