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# On the instability of emulsions made with surfactant-oil-water systems at optimum formulation with ultralow interfacial tension

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## Abstract

We have studied emulsions made with two and three-phase oil-water-surfactant systems in which one of the phases is a microemulsion, the other phases being water or/and oil excess phases. Such systems have been extensively studied in the 70-80's for applications in enhanced oil recovery. It was found at that time that the emulsions became very unstable in the three-phase systems, but so far few explanations have been proposed. In the most complete one, Kabalnov and colleagues related the emulsion stability to the probability of hole nucleation in the liquid film separating two nearby emulsion drops, and associated this probability to the curvature elastic energy of the surfactant layer covering drop surfaces. We propose a different explanation, linked to another type of interfacial elastic energy, associated to compression of the surfactant layers. As found long ago, the three-phase systems are found near optimum formulation (Hydrophile Lipophile Difference HLD = 0), where the interfacial tension exhibits a deep minimum. The determination of interfacial elastic properties in low interfacial tension systems is not straightforward. In our present work, we used a spinning drop tensiometer with an oscillating rotation velocity. We show that the interfacial compression elastic modulus and viscosity also exhibit a minimum at optimum formulation. We propose that this minimum is related to the acceleration of the surfactant exchanges between the interface, oil and water, near the optimum formulation. Furthermore, we find that the surfactant partitions close to equally between oil and water at the optimum, as in earlier studies. The interfacial tension gradients that slow down the thinning of liquid films between drops are reduced by surfactant exchanges between drops and interface, which are fast whatever the type of drop, oil or water; film thinning is therefore very rapid and emulsions are almost as unstable as in the absence of surfactant.

**Key words:** Winsor systems, microemulsions, low interfacial tension, emulsion stability, interfacial rheology,

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## Introduction

Emulsions are dispersions of oil and water stabilized by surface active agents, either surfactants which are small molecules, larger molecules such as polymers and proteins, or particles (Pickering emulsions)<sup>1</sup>. Despite its practical importance, emulsion stability is far from being fully understood. Empirical rules are still used for formulation purposes, such as the HLB parameter (hydrophilic-lipophilic balance). Significant improvements were obtained with the HLD parameter (hydrophilic-lipophilic deviation) introduced by Salager and his colleagues. The HLD takes into account in a simple way many variables such as surfactant, oil and water type, as well as temperature<sup>2,3</sup>, and even pressure<sup>4</sup>. However, no easily accessible parameter predicts yet emulsion stability.

Emulsions destabilize because of one or more of the following processes:

- sedimentation or creaming, due to the action of gravity on the oil or water drops.
- Ostwald ripening, produced by diffusive transfer of liquid between drops due to pressure differences.
- coalescence (fusion) of droplets during encounters

All droplets encounters may not be followed by coalescence, and in very stable emulsions, the two first processes have time to proceed before complete emulsion destabilization. In turn, unstable emulsions destabilize mainly through coalescence.

The three processes listed above could involve many different mechanisms. Among others, viscosity or viscoelasticity of the liquid phases affect them in different ways. For instance, the presence of surfactant lamellar phases leads to very stable emulsions<sup>5</sup>. When the surface active agents are particles (Pickering emulsions), they form very rigid interfacial layers and the emulsions may be very stable<sup>6</sup>. In this article, we will restrict the topic to emulsions made with similar volumes of water and of non-viscous oils and small quantities of a pure surfactant, in order to simplify the discussion. Furthermore, we will focus on low interfacial tension systems which have other specific properties. We will present measurements of interfacial tension and of interfacial compression elasticity in mixtures of brine, oil and an ionic surfactant, using a new instrument, the oscillating spinning drop tensiometer<sup>7</sup>. The interfacial tension is found to strongly vary by changing the amount of salt in water. In this way, an interfacial tension minimum is obtained at an *optimum salinity*. The interfacial compression parameters are also minimum. This feature has been reported for the first time in a recent study with various types of commercial surfactants, ionic and nonionic<sup>8</sup>. It had been ignored so far because of the lack of suitable instruments allowing interfacial rheology measurements with low tension systems. In the present study, we used a pure surfactant that allows us to discuss in depth the behaviour of interfacial rheology and to relate it with emulsion stability.

## Background

### Winsor systems

The interfacial tension  $\gamma$  between oil and water is currently about 30-50 mN/m. When suitable surfactants are used, it can be lowered to 0.01 mN/m or less. Stable systems called *microemulsions*, made of very small oil or water drops, can be then obtained. Microemulsion droplets are much smaller than emulsion drops, implying a higher surface energy ( $\gamma$  times total interfacial area). The number of droplets is however larger than in emulsions and the dispersion entropy compensates the surface energy. The same compensation occurs in microemulsion bicontinuous structures, made of small interconnected domains that form in some particular cases. As a result, microemulsions are thermodynamically stable<sup>9</sup>.

The type of droplet formed is related to the spontaneous curvature  $C_0$  of the surfactant layer: if by convention  $C_0 > 0$ , oil droplets are formed and if  $C_0 < 0$ , water droplets are formed. The spontaneous curvature is itself related to the surfactant geometry, as pointed out by Tanford<sup>10</sup>. Israelachvili, Mitchell and Ninham introduced later a *packing parameter* in order to quantify this surfactant geometry<sup>11</sup>. The actual curvature  $C$  is in general different from  $C_0$ , and is associated to a curvature energy as proposed by Helfrich<sup>12</sup>

$$E_{\text{curv}} = \frac{1}{2} K (C_1 + C_2 - 2C_0)^2 + \bar{K} C_1 C_2 \quad (1)$$

where  $K$  and  $\bar{K}$  are respectively the mean and gaussian bending moduli,  $C_1$  and  $C_2$  are the two principal curvatures of the surfactant layer (for droplets of radius  $R$ ,  $C_1 = C_2 = 1/R$ )

When oil is added to an oil in water (O/W) microemulsion, the drops grow until their curvature reaches  $C_0$ , after which excess oil separates into an oil phase in order to minimize the curvature energy: this phenomenon was called *emulsification failure*<sup>13</sup>. A similar behaviour is observed with water in oil (W/O) microemulsions that coexist with excess water once  $C_0$  is attained. The case  $C_0 \sim 0$  is peculiar, the corresponding microemulsions coexisting with both excess oil and water. Their structure is not made of droplets, but is rather sponge-like, bicontinuous in oil and water, with oil and water domains separated by surfactant monolayers<sup>14</sup>. The typical size in this case is not the inverse spontaneous curvature; it is smaller due to thermal fluctuations and is equal to the persistence length  $\zeta$  of the surfactant layer:  $\zeta \sim b \exp(2\pi K/k_B T)$ ,  $b$  being a molecular length  $k_B$  the Boltzmann constant and  $T$  the absolute temperature<sup>9</sup>.

These three different phase equilibria were described by Winsor in the 50's and called after him Winsor I (O/W microemulsion in equilibrium with excess oil), Winsor II (W/O microemulsion in equilibrium with excess water) and Winsor III (bicontinuous microemulsion in equilibrium with excess oil and water). These systems attracted much interest in the 70-80s for enhanced oil recovery (EOR) applications. Indeed, the interfacial tensions between the different phases are very low, allowing for efficient release of oil trapped in the pores of the oil reservoirs, by reducing capillary pressures. The lowest tensions were found in the Winsor III region, and research to formulate such systems became active. Formulation variables were identified and include surfactant type, water salinity, oil nature and temperature. When changing a single variable in so-called formulation scans, interfacial tension minima were systematically found in the Winsor III region corresponding to physicochemical conditions which were referred to as the *optimum formulation*<sup>15 16</sup>.

## Emulsion stability

The three emulsion destabilization processes mentioned in the introduction, sedimentation, ripening and coalescence occur simultaneously and are coupled: for instance if the drop size increases because of coalescence, sedimentation will be faster. The fastest step is usually drops approach. If coalescence occurs during this approach, the emulsion is very unstable. This is the case of oil and water mixtures without surfactant. When surfactant is present and its concentration not too small with respect to the *critical micellar concentration* ( $C_{mc}$ ), the coalescence probability decreases and sedimentation has time to proceed. As a result, a sedimentation (or creaming) front appears between the continuous phase and a more concentrated emulsion that moves downwards (resp. upwards). The motion is accelerated in the case of drop flocculation, frequent in water in oil emulsions<sup>1</sup>. The front motion slows down considerably once the drops are compacted and touch each other, and the drop volume fraction reaches the value for random close packing of spheres (~64%). These compacted emulsions are solid-like (they do not flow) and are frequently called *creams*. Ostwald ripening and coalescence lead to the growth of drops and to another phase separation, this time between the emulsion and the released internal phase.

While the theoretical description of sedimentation (or creaming) and of Ostwald ripening is well advanced, coalescence is much less well understood. Different mechanisms can lead to drop fusion. When emulsions are very unstable (lifetimes of a few minutes), the drops approach rapidly (due to buoyancy, Brownian motion or another applied body force), a liquid film is formed between them (unless they are very small) which thins rapidly if the compression elastic modulus is small<sup>17</sup>. Note that this modulus is different from the curvature elastic moduli introduced in the section *Winsor systems*<sup>18</sup>. If the amount of surfactants is small, the compression modulus is small and cannot prevent film instability, coalescence is then rapid. In these cases, the emulsions have no time to reach a compact state. With more stable emulsions (lasting for more than a few hours), instabilities may still occur, but do not necessarily lead to film rupture. The emulsions then reach the compact state, films form between drops and the film thickness stabilizes at an equilibrium value determined by the balance between the external force (capillary pressure due to the curvature of film borders and gravity, generally smaller) and the force between film surfaces, which, counted per unit area, is called *disjoining pressure*<sup>19</sup>. In Winsor systems, the surfactants used are either non-ionic, or ionic generally in the presence of large amounts of salt (with only a few exceptions<sup>20</sup>), meaning that the disjoining pressure  $\Pi_d$  only contains repulsive contributions from short range forces, steric and hydration : the equilibrium film thickness is very small, of the order of 5nm.

The rupture of these very thin films, called *Newton black films*, remains mysterious. This rupture is possibly controlled by thermally activated hole nucleation in the film, as proposed by de Vries<sup>21</sup> and later by Exerowa et al<sup>22</sup>. The energy barrier associated to the nucleation process is the surface energy cost and is large. This led de Gennes to postulate later on that this type of intrinsic coalescence is a myth<sup>23</sup>. However, in systems with low interfacial tensions, the energy cost is smaller, as shown by Kabalnov and Wennerstrom<sup>24</sup>. These authors addressed the case of the rather stable cream emulsions and highlighted the importance of the interfacial *curvature* elastic energy. However, their model is not suitable to emulsions that destabilize in minutes when the interfacial tension is ultralow. Another type of interfacial elasticity might then become important, the *compression* elasticity, which controls the surfactant mobility on emulsion drop and film surfaces.

Winsor systems can be emulsified as other oil-water-surfactant systems. The emulsions made with Winsor I and II systems have a fair to good stability. In the WI (respectively WII) systems, most of the surfactant is in the water (respectively oil) phase and an O/W (respectively W/O) emulsion is formed. This is in agreement with the Bancroft rule that states that the emulsion that forms is the one for which the continuous phase contains the surfactant<sup>25 26 27</sup>. The inversion from O/W to W/O emulsion occurs in the WIII region, as evidenced from electrical conductivity studies and coincides with the minimum in interfacial tension. It was also recognized that there is a considerable change in emulsion stability when moving away from the interfacial tension minimum, even in regions where creams form. Emulsions are also obtained with Winsor III systems, but in this case the stability is very poor and the emulsion destabilizes in a few minutes, leading back to the equilibrium three phases. The first clear observations were made in 1979-1980<sup>28 29 30</sup>. Most papers show a strong decrease in emulsion stability close to the interfacial tension minimum<sup>31 28 32 33</sup>. Some studies went further and correlated the stability minimum with the inversion from an O/W to a W/O emulsion<sup>29 34 35 36 37 33</sup>. A few studies investigated the link between coalescence and interfacial elasticity, but of still different type (*shear*)<sup>38 39 40</sup>. Boyd and coworkers showed that the elastic shear modulus had more influence than the interfacial shear viscosity, but the change in stability of the emulsions with temperature was much larger than that of the interfacial shear parameters. Hazlett and Schechter proposed that the reduced stability close to the interfacial tension minimum was due to the presence of microemulsion structures that could percolate into the thin emulsion films and rupture them<sup>37</sup>. It was shown later however that the presence of the microemulsion was not necessary and that the emulsion low stability was the same if it is removed<sup>36</sup>. The stability of emulsions made with these systems was related to the interfacial curvature elasticity by Kabalnov *et al*<sup>24 41</sup>. It is however mentioned by Kabalnov and Wennerstrom that their model is limited to the case of “stable” emulsions which lifetimes are on the order of hours or more. They write in ref<sup>24</sup>: *the short-term rupture may be dependent on film thinning hydrodynamics and hydrodynamic stability while the long-term stability is controlled predominantly by hole nucleation in emulsion film*.

In the following, we will recall in more detail the general knowledge concerning emulsion stability, distinguishing the case of stable and unstable emulsions, which rely on different mechanisms.

### Case of long lifetimes

Kabalnov and Wennerstrom calculated the coalescence energy barrier  $W^*$  and found a strong dependence on the monolayer spontaneous curvature. They modelled polyethoxylated nonionic surfactant-oil-water mixtures in which the evolution from WI to WII systems is obtained by increasing temperature. For the octane-C<sub>10</sub>E<sub>5</sub>-water system, they found that close to the temperature  $T^*$  at which the interfacial tension is minimum,  $W^*/k_B T$  is equal to  $0.43 + 30.9 \Delta T$  with  $\Delta T = |T - T^*|$ . Farther from  $T^*$  (but  $\Delta T \leq 5^\circ$ ),  $W^*/k_B T$  approaches values equal to about 40. They however used values of  $\bar{K}$  and  $\bar{\bar{K}}$  deduced from an incomplete fit of interfacial tension data:  $\bar{K} = 0.6 k_B T$  and  $\bar{\bar{K}} = 0.3 k_B T$ , while the correct values are rather  $\bar{K} = k_B T$  and  $\bar{\bar{K}} = -0.36 k_B T$ <sup>42</sup> leading to  $W^*/k_B T \sim 11.5 + 41.8 \Delta T$ . The variation of  $W^*$  is more important than stated, and would lead to an increase in emulsion stability three times larger than observed. But in view of the uncertainties on the values of  $\bar{K}$  and  $\bar{\bar{K}}$ , the model could well still account for the observations.

Another model of hole opening has been proposed by de Gennes, who related the energy barrier to the compression elastic energy. This model could explain why the stability of emulsions frequently

appears correlated with the interfacial compression modulus  $E$ . He estimated the energy barrier as <sup>23</sup>  
<sup>43 44</sup> .

$$W = E \left[ \frac{\Delta\Gamma^2}{\langle\Delta\Gamma^2\rangle} \right] S \quad (2)$$

where  $S$  is the hole area,  $\Gamma$  the surface concentration in the surfactant monolayer,  $\Delta\Gamma$  its variation and  $\langle\Delta\Gamma^2\rangle$  the mean square amplitude of these variations due to thermal fluctuations.

When a surface layer is compressed, it resists compression with an elastic force characterized by a compression modulus given by:

$$E = -A \frac{\partial\Pi}{\partial A} \quad (3)$$

where  $\Pi$  is the surface pressure, equal to the difference between interfacial tensions with and without surfactant, and  $A$  is the surface area <sup>45</sup>. The modulus  $E$  is also called *dilational* or *dilatational* modulus in the literature. Assuming that when compressed, the surfactant remains at the interface,  $\Gamma$  is inversely proportional to  $A$  and :

$$E = \Gamma \frac{\partial\Pi}{\partial\Gamma} \quad (4)$$

The mean square value of  $\Delta\Gamma$  in equation 2 is then  $\langle\Delta\Gamma^2\rangle \sim k_B T \Gamma^2 / E S$ .

De Gennes showed that when a film ruptures, the critical radius of the hole  $r^*$  is half the film thickness <sup>43</sup>. The critical hole radius being half the film thickness, is of the order of the surfactant size in Newton black films:  $r^* \sim 2$  nm. The compression modulus  $E$  is close to twice the surface pressure of the monolayer or smaller <sup>46 47 48</sup>. We will use here a maximum value of 100 mN/m. The remaining term in equation 2 can be estimated as  $\Delta\Gamma \sim \Gamma$ , in which case the hole surfaces are free of surfactant before hole opening. The coalescence barrier  $W^*$  is then of the order of  $100 k_B T$ .

This led de Gennes to assert that the nucleation of holes in surfactant rich systems was forbidden. However, it is probably not necessary to have a fully bare surface before film rupture. It is well known that emulsions become stable when the surfactant concentration  $C$  reaches a value  $C^*$ , somewhat below the critical micellar concentration ( $Cmc$ ) and close to the point below which the surface concentration starts decreasing appreciably <sup>49</sup>. At these concentrations, the repulsive forces disappear and no equilibrium film is formed <sup>50</sup>. This means that  $\Delta\Gamma$  in equation 2 can be smaller than  $\Gamma$  for the hole to nucleate. If we take for instance  $\Delta\Gamma \sim \Gamma/3$ , the energy barrier  $W^*$  falls to  $30 k_B T$ , i.e. even smaller than that estimated for the curvature energy contribution only one degree away from the interfacial tension minimum in the  $C_{10}E_5$ -octane water system.

### *Case of short lifetimes*

In short life emulsions, two drops that collide fuse shortly afterwards, and creamed emulsions have no time to form. Upon approach, the drops start deforming and a film of uniform thickness may form between them, depending on their relative velocity and size, as well as on the disjoining pressure. The film may also have a dimpled shape, in which case, it will thin more slowly provided it remains axisymmetrical <sup>51</sup>. The velocity of film thinning depends on the mobility of film surfaces: if they are rigid-like, the thinning velocity is controlled by bulk viscosity, and if the surfaces are mobile, the velocity becomes very large, being controlled by inertia <sup>52</sup>. In the intermediate case, film drainage is

closely related to interfacial rheology: indeed, when a film thins, the surfactant at the film surfaces is entrained, surface concentration gradients arise and create interfacial tension gradients. This results in huge forces opposing film thinning (Marangoni forces), which magnitude is related to the interfacial elastic modulus  $E$ . Interfacial viscosity can also limit the surfactant motion and slow down thinning. Theories relating the thinning velocity to interfacial rheology have been proposed<sup>53 54</sup>.

In concentrated surfactant solutions, the resistance to compression is generally lowered by dissolution of surfactant in the bulk. The interfacial motion is then described by an effective compression modulus, smaller than  $E$ . The exchanges between bulk and interface result in a large dissipation and the resistance to compression includes both an elastic contribution, characterized by a *storage modulus*  $E_{eff}'$ , and a viscous contribution, characterized by a *loss modulus*  $E_{eff}''$ . If we consider for instance the case of air-water interfaces in quiescent conditions, and a sinusoidal compression with a frequency  $\omega$ , the effective storage and loss moduli in the linear regime are given by a *diffusion model*<sup>45 55</sup>

$$E_{eff}' = E \frac{1+\Omega}{1+2\Omega+2\Omega^2} \quad (5)$$

$$E_{eff}'' = E \frac{\Omega}{1+2\Omega+2\Omega^2} \quad (6)$$

$$\Omega = \frac{1}{\sqrt{\omega\tau_D}} = \sqrt{\frac{D}{2\omega}} \frac{\partial C}{\partial \Gamma} \quad \text{with} \quad \tau_D = \frac{2}{D} \left( \frac{\partial \Gamma}{\partial C} \right)^2 \quad (7)$$

where  $D$  is the surfactant diffusion coefficient in bulk;  $E_{eff}'$  is equal to  $E$  at high frequencies, and tends to zero when  $\omega$  become small, while  $E_{eff}''$  tends to zero at both small and large  $\omega$ .

In liquid films, the situation can be different, in particular when the film thickness  $h$  falls below  $h^* \sim \Gamma/C$ . Indeed, during film thinning, the surfactant is dragged along the film border and when  $h < h^*$ , there is not enough surfactant in the film to replenish the film surfaces (see figure 1). Because there are no longer exchanges between bulk and surfaces, the surfactant layer behaves as if it were insoluble and the elastic modulus to be considered is the intrinsic modulus given by equation 4. Film thinning studies confirmed this picture<sup>17</sup>. The situation is different if the surfactant is solubilized in the droplets: in this case the interface is easily replenished during film thinning, and the modulus to be considered is that given by equation 5 for a frequency  $\omega$  of the order of the inverse thinning time, much smaller than  $E$  in general. It has been indeed observed that the thinning of air films in surfactant solutions is much faster than the thinning of films of the same surfactant solutions in air<sup>56</sup>. In the case of low interfacial tension systems, it has also been shown that the lifetimes of drops colliding the oil-water interfaces depended on the type of drops: oil drop lifetimes were longer than those of water drops in the WI region and the reverse was observed in the Winsor II region<sup>57</sup>. This behavior was predicted by Hildebrand in order to account for the Bancroft rule<sup>25</sup>

Note that interfaces between pure fluids are most of the time contaminated by small amount of surface active impurities and counterintuitively behave as rigid : there is not enough contaminant to replenish surfaces and even very small surface tension gradients can stabilize the interface<sup>52</sup>. When sufficient surfactant is present, the interfaces are easily remobilized and can behave as mobile ones<sup>58</sup> (excepted in confinement situations such as in thin films, as discussed above).



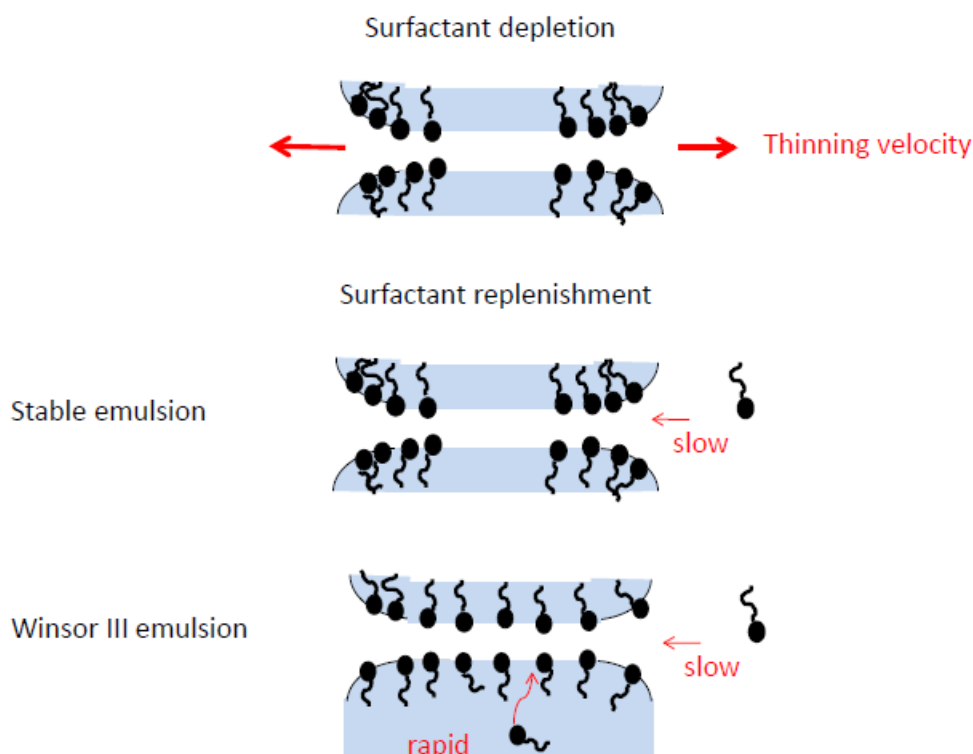


Figure 1. Schematic of surfactant motion during the approach of two emulsion drops (in blue color). In the two top figures, the film surfaces in the central region are completely depleted in surfactant in order to appreciate better the contrast with the bottom figure

The faster the film thinning, the easier is the occurrence of instabilities. The development of asymmetrical instabilities leading to rapid rupture is frequent in films with small interfacial elastic and viscous moduli<sup>51-59</sup>. This is likely because the surfactant is locally displaced, hence the repulsive forces between surfaces vanish, only attractive van der Waals forces are left and rupture follows. The instabilities prevent the formation of the thin equilibrium films, hence the hole nucleation mechanism discussed in the section *case of long lifetimes* cannot take place.

### Interfacial compression rheology

When a surface layer is compressed, it resists compression with an elastic force characterized by a modulus  $E$  when the compression is fast enough and surfactant dissolution had no time to proceed. When the compression is slower, the resistance is smaller and includes elastic and viscous contributions. When the exchanges between interface and bulk are governed by diffusion, these contributions can be calculated using equations 5 and 6. The storage modulus is equal to the intrinsic modulus  $E$  at high frequencies and approaches zero at low frequencies. The loss modulus is zero at both high and low frequencies but is large and of the order of  $E/5$  when  $\Omega \sim 1$ . The corresponding interfacial viscosity is huge:  $\eta_E \sim E_{int}''/\omega$ , much larger than intrinsic interfacial viscosities of surfactant layers<sup>60</sup>.

In practice, the intrinsic compression modulus  $E$  can be calculated when the variation of the interfacial tension with concentration is known. Indeed one can then deduce the surface concentration  $\Gamma$  using the Gibbs equation:

$$\Gamma = - \frac{1}{k_B T} \frac{\partial \gamma}{\partial \ln C} \quad (8)$$

for a nonionic surfactant or an ionic surfactant in the presence of excess salt. Note that this equation can only be used below the critical micellar concentration ( $Cmc$ ), because above this concentration, micelles form and the surface tension remains constant<sup>19</sup>. In general, the surface concentration reaches a limit value  $\Gamma_\infty$  close to the  $Cmc$ <sup>61</sup>. Above the  $Cmc$ , micelles are present, and the exchange time between micelles and surface can become limiting. Equations 5-7 then need to be modified<sup>62</sup>. These equations were also generalized for binary surfactant mixtures, including soluble and insoluble surfactants<sup>63</sup> and surfactant partitioning between oil and water<sup>64</sup>. In the case of ionic surfactants and low ionic strength, equations 5-7 are not valid and more complex treatments are necessary<sup>65</sup>.

The relation between equilibrium bulk and surface concentrations is frequently approximated by the *Langmuir equation*:

$$\frac{C}{a} = \frac{\Gamma/\Gamma_\infty}{1-\Gamma/\Gamma_\infty} \quad (9)$$

where  $a$  is the *Szyszkowski* concentration, smaller than the  $Cmc$ . One can see from equation 9 that the derivative  $d\Gamma/dC$  becomes very small when  $\Gamma$  approaches  $\Gamma_\infty$ , meaning that the characteristic frequency  $\Omega$  becomes high and the elastic modulus  $E$  small. More complex expressions incorporate interactions between molecules at the surface, such as the Frumkin equation and others. However, surfactants at oil-water interfaces are usually well described by equation 9<sup>66</sup>.

The equipment used for measuring the interfacial compression rheology is mainly based on the oscillating pendant drop and oscillating barrier methods<sup>67</sup>. Instruments are commercially available and can be used at low frequencies, 1Hz and below<sup>68</sup>. However, they are not suitable for systems with interfacial tensions below a few mN/m: the pendant drops detach from the holding capillaries and the barrier methods make use of interfacial tension measurements with transducers that are not sensitive enough to measure very low tensions. Another drop method, called spinning drop technique, and developed in the 70s in the University of Texas at Austin<sup>69</sup>, was extensively used for the study of low interfacial tensions in Winsor systems. The idea of oscillating the area of a spinning drop was proposed by Slattery<sup>70</sup> and implemented in a new instrument developed by the FIRP Laboratory and CITEC workshop at the Universidad de Los Andes (ULA), Mérida-Venezuela. With this apparatus, the surface rheological properties can be measured for systems with interfacial tensions as low as  $10^{-3}$  -  $10^{-4}$  mN/m<sup>7</sup>.

## Materials and methods

### Chemicals and sample preparation

The surfactant used is sodium dodecyl benzene sulfonate (SDBS), an anionic surfactant, from Sigma-Aldrich, USA. The oil is cyclohexane, technical grade, provided by Fisher Scientific. Water is MilliQ water containing sodium chloride (NaCl), analytical grade, from Merck, Germany. We have also used a short chain alcohol (co-surfactant), known to increase the fluidity of the interfacial layers. We

chose sec-butanol (reactive grade, from Scharlau) that has the advantage of bringing minimum changes of the HLD, and therefore does not significantly affect the formulation <sup>71</sup>.

Equal volumes (5 mL) of cyclohexane and of the aqueous phases containing the surfactant and NaCl were contacted while placed into graduated test tubes. They were very slightly shaken and then allowed to stand 24 h in a thermostatic bath at 30 °C until equilibrium was reached. The salinity of the aqueous phase was varied from 2.75 to 5 wt% NaCl (corresponding to 0.47-0.9 M). The surfactant concentration used is 0.02 wt%, close to the *Cmc*. We chose a low surfactant concentration in order to slow down diffusion and to minimize exchanges between bulk and interface. In this way, the measured moduli are expected not to be too small. Another advantage is to limit the formation of microemulsions. With this low surfactant concentration indeed, very small amounts of middle phase were visible close to optimal salinity (none in the absence of alcohol). The alcohol concentration, when used, is 1 wt%. The amount of surfactant in aqueous and organic phases was measured with a UV-visible spectrometer.

The HLD can be obtained simply using the reported parameters for the SDBS/cyclohexane/brine system <sup>71 72 73</sup>:

$$\text{HLD} = \ln S - k \text{ ACN} + f(A) + \sigma - a_T \Delta T = 0 \quad (10)$$

where  $\Delta T$  is the temperature difference with respect to 25°C. In the studied system,  $T = 30^\circ\text{C}$ ,  $\sigma = -0.60$ ,  $k = 0.16$  for sulfonate anionic surfactants,  $\text{EACN} = 3.5$  for cyclohexane,  $a_T = 0.01$ ;  $f(A)$  is a term depending on the alcohol co-surfactant, here  $f(A) \approx 0$ .

### Emulsion stability.

Emulsions were obtained by mixing equal volumes of oil and surfactant aqueous solutions. The two liquids were pre-equilibrated for a period of 24 h and then mixed with an Ultraturrax blender at 30000 rpm for 30 s. We measured the time necessary for the separation of 60% of the aqueous and oil phases. In WI systems, resolution of water is due to microemulsion drop creaming, while oil resolution is due to coalescence. The reverse occurs in WII systems.

### Interfacial tension and interfacial rheology measurements with an oscillating spinning drop apparatus

The determination of interfacial tension and interfacial area of the drop by means of the spinning drop method is based on the axial elongation of an oil drop in the aqueous phase. The interfacial tension is determined using Vonnegut's equation <sup>74</sup>

$$\gamma = 0.25 \Delta\rho \omega_{rot}^2 r^3 \quad (11)$$

where  $\gamma$  is the interfacial tension,  $r$  is the radius of the droplet at central equator,  $\Delta\rho$  is the density difference between the two fluids, and  $\omega_{rot}$  is the rotational velocity. This equation is valid for sufficiently elongated drops, i.e. longer than 4 times their diameter.

This method can be used to measure interfacial rheology, by modulating the rotation frequency, i.e. expanding or contracting the drop during its rotation <sup>7</sup>. The effective interfacial compression modulus  $E_{eff}$  is calculated using:

$$E_{eff} = A_0 \frac{\Delta\gamma}{\Delta A} \quad (12)$$

where  $\Delta\gamma$  is the change in interfacial tension,  $\Delta A$  is the amplitude of variation of the area and  $A_0$  is the initial area of the drop. The phase angle is the phase difference between the sinusoidal curves of the interfacial tension and area. The storage elastic modulus is  $E_{eff}' = E_{eff} \cos\phi$  and the loss modulus is  $E_{eff}'' = E_{eff} \sin\phi$ .

A Spinning Drop Oscillatory Interfacial Rheometer, model RI-1000 (FIRP Laboratory-CITEC, ULA, Venezuela) <sup>7</sup> was used to perform the interfacial rheological measurements. The interfacial elastic moduli were determined using the previously equilibrated systems (during 24 hours). A drop of oil phase is placed in a capillary containing the aqueous phase. The temperature is controlled at 30° C. The rotational speed and consequently the drop area are varied sinusoidally at a frequency  $\omega = 0.1$  Hz in the experiments presented in this paper. The oscillation amplitude was maintained below 10%, which guarantees that the response is linear. This oscillation amplitude was generally 1000 rpm, the selected rotating speed variation according to the interfacial tension (the lowest values being 3000 to 4000 rpm for ultralow interfacial tensions).

## Results

At low salinity, a WI two-phase system is obtained; the surfactant-rich phase is the lower aqueous phase and the oil phase is the upper phase. At high salinity, the surfactant-rich phase is the upper oil phase. The corresponding emulsions are of O/W and W/O type respectively. They are associated to Winsor type I and II equilibria far from optimal salinity (figure 2). The time needed to reach equilibrium for the interfacial tension measurements was about 15 min for systems without alcohol and 5 min for systems containing sec-butanol.

The amount of surfactant in the aqueous and oil phases is given in Table 1, for systems without and with alcohol. One sees in table 1 that the surfactant partition coefficient  $k$  is close to one in the three-phase region for the system containing alcohol. This is as observed previously with other ionic surfactant systems <sup>75</sup>, including commercial mixtures <sup>69, 76 77</sup>, and first reported by Salager <sup>78</sup>. It is close but smaller than one in the system free of alcohol. Note that in this case, the surfactant becomes insoluble in water and precipitates just above 5 wt% NaCl. In both cases, the sum of the amounts present in oil and water phases is equal to the total amount of surfactant (0.02 wt%) within error bar.

%NaCl	0% sec-butanol			1 % sec-butanol		
	% SDBS in water	% SDBS in oil	k	% SDBS in water	% SDBS in oil	k
2.75	0.0135	0.007	0.52	0.0131	0.0065	0.50
3	0.0133	0.0078	0.59	0.0131	0.006	0.46
3.25	0.0131	0.0076	0.58	0.0122	0.0077	0.63
3.5	0.0126	0.0084	0.67	0.0112	0.0064	0.57
3.75	0.0115	0.0075	0.65	0.0101	0.0098	0.97
4	0.0107	0.0078	0.79	0.0097	0.0104	1.07
4.25	0.0102	0.0081	0.79	0.0095	0.0105	1.11
5	0.0094	0.0082	0.87	0.0088	0.0104	1.18

Table 1. Amount of surfactant in the aqueous phases for systems without and with alcohol. Brine-cyclohexane-SDBS-sec-butanol mixtures.

Figure 2 shows the aspect of the samples containing alcohol. A very small amount of middle phase (volume fraction less than 1%) is visible in the systems close to optimum formulation at HLD=0. The phases in samples containing no alcohol are fully transparent.

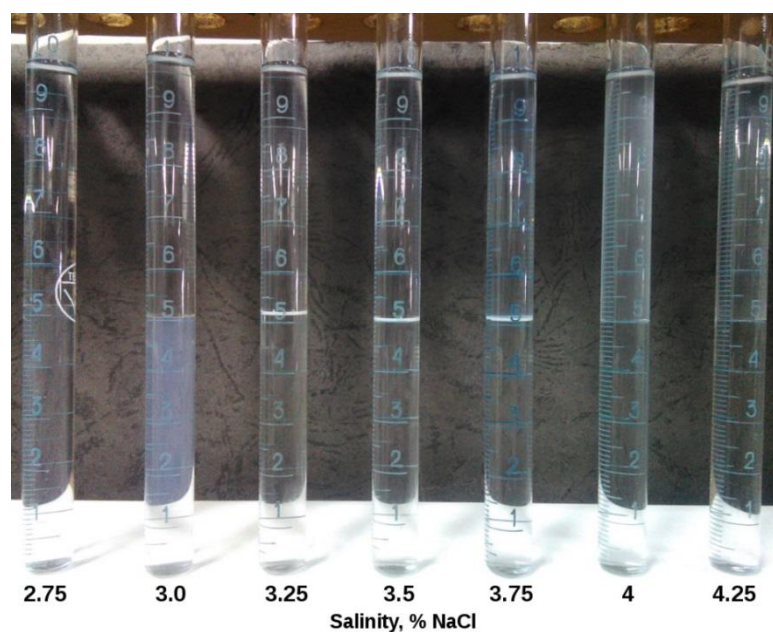


Figure 2. Aspect of the systems containing alcohol at equilibrium. NaCl (wt%) concentrations indicated at the bottom. Brine-cyclohexane-SDBS-sec-butanol mixtures.

### Interfacial properties measurements.

Figure 3 represents the interfacial tension  $\gamma$ , interfacial effective modulus  $E_{eff}$  and phase angle  $\phi$  for systems with and without alcohol, as a function of the aqueous phase salinity. The optimal salinity is 3.50 % NaCl without alcohol and slightly larger, i.e. 3.75 % NaCl with alcohol, in line with the very slight effect of sec-butanol on optimum formulation<sup>71</sup>. The salinity at optimum formulation calculated with equation 10 is  $S^*=3.4$  % NaCl, which is a fairly good agreement with the measured

values. The small deviations with respect to the measurements could be due to residual impurities in the chemicals used. The HLD = 0 data points are indicated with a star in figures 3 and 5.

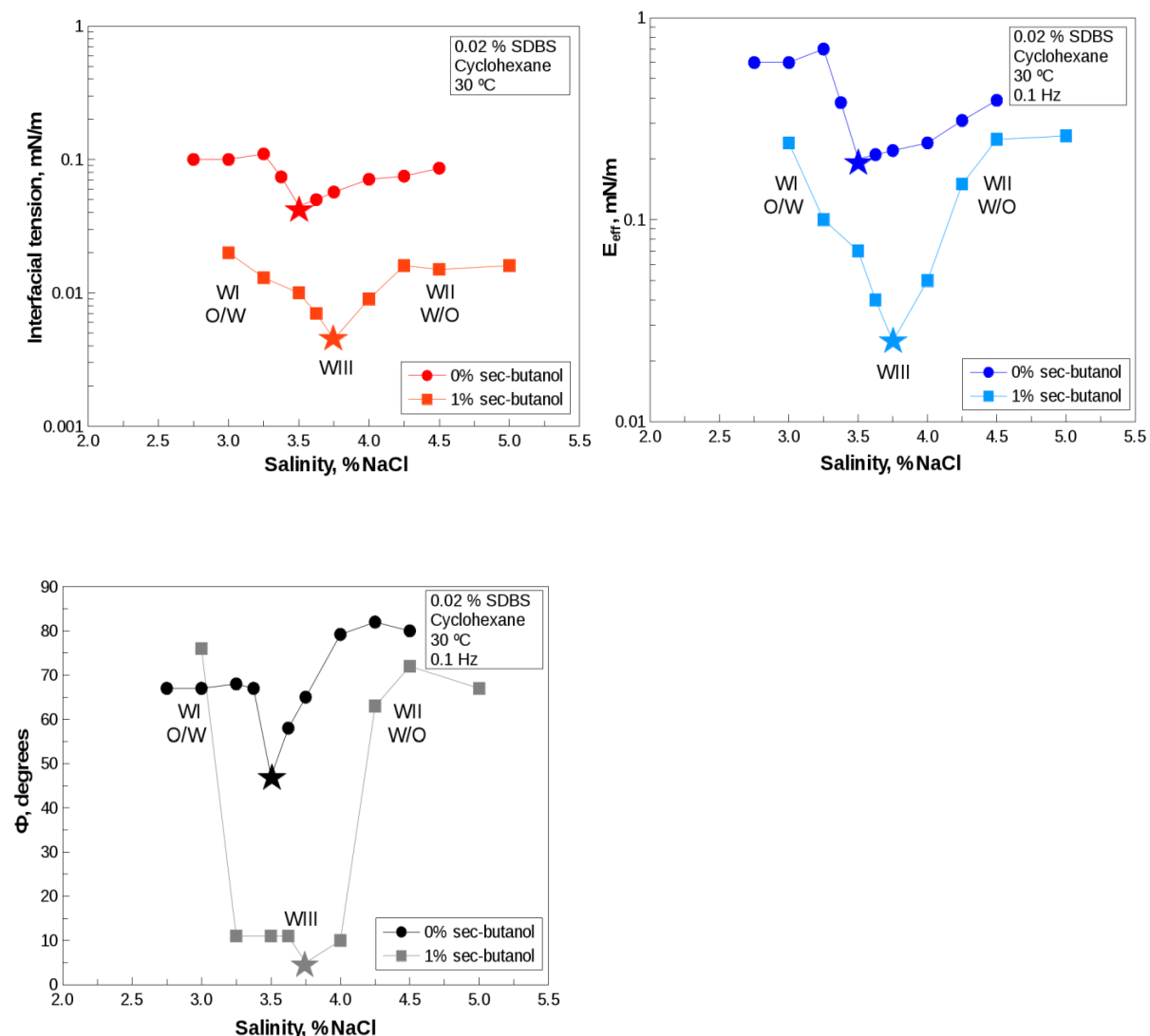


Figure 3. Interfacial tension  $\gamma$  (top left), interfacial effective elastic modulus  $E_{eff}$  (top right), and phase angle  $\phi$  (bottom) as a function of salinity as formulation scan variable. Brine-cyclohexane-SDBS-sec-butanol mixtures, SDBS concentration 0.02 wt%,  $T=30$  °C. Circles: alcohol-free systems; squares: systems containing 1 wt% sec-butanol. The lines are guides to the eye

As usual in this type of systems, an interfacial tension minimum is observed at optimal salinity (Figure 3 top left). The interfacial rheological parameters also show a minimum at optimal salinity. The amount of surfactant in both oil and water is small but sufficient to replenish the surface when stretched. Because of this small amount, the replenishment being controlled by diffusion is slow and the effective elastic modulus is therefore small, but non-zero. The fact that  $E_{eff}$  is minimum for HLD=0 suggests that the exchange times are the shortest at this point.

The interfacial tension was measured as a function of surfactant concentration, in order to obtain the value ( $C_{\mu c}$ ) above which a middle phase appears for the systems with HLD=0. Figure 4a and b are in

log-log and linear-log units respectively. Figure 4b allows visualizing the position of the  $C_{\mu c}$ , while Figure 4a shows that the tension continues to decrease slowly above the  $C_{\mu c}$  and reaches ultralow values. The modulus and the phase angle were also measured and the data is shown in figure 4c and 4d.

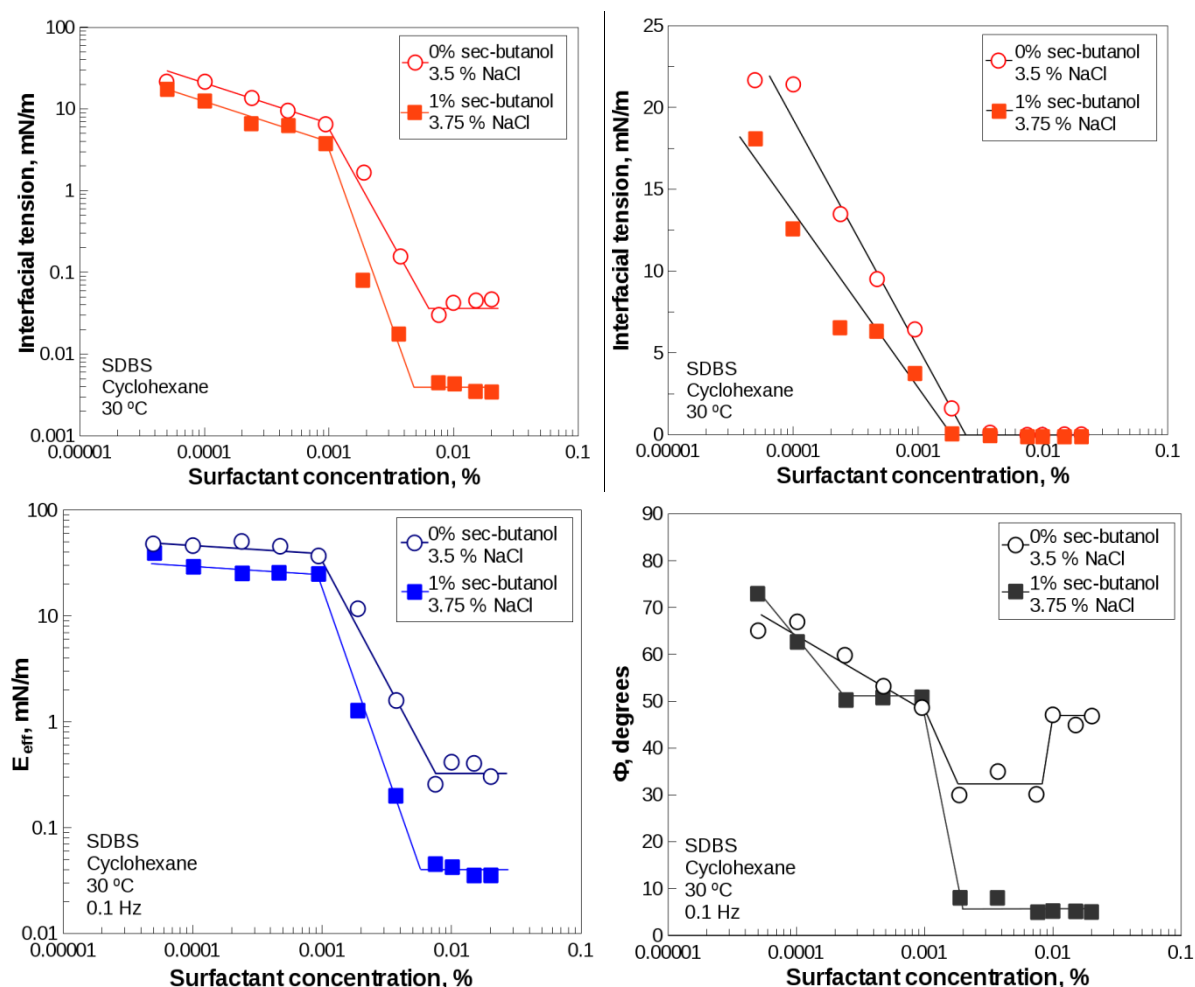


Figure 4. Interfacial tension versus surfactant concentration in log-log units (top left) and linear-log units (top right). Effective modulus (bottom left) and phase angle (bottom right) versus surfactant concentration. Data at optimal salinity,  $S = 3.50\%$  for alcohol-free samples and  $3.75\%$  with alcohol ( $HLD=0$ ). Brine-cyclohexane-SDBS-sec-butanol mixtures. Open circles: alcohol-free systems; closed squares : systems containing 1 wt% sec-butanol. The lines are guides to the eye.

Note that the optimal salinity may vary with surfactant concentration<sup>69</sup>, and that only the data for 0.02 wt% SDBS corresponds strictly speaking to the optimal salinity.

### Emulsion stability measurements

Figure 5 shows the variation of emulsion stability evaluated as the time of separation of 60% of water or oil versus salinity.

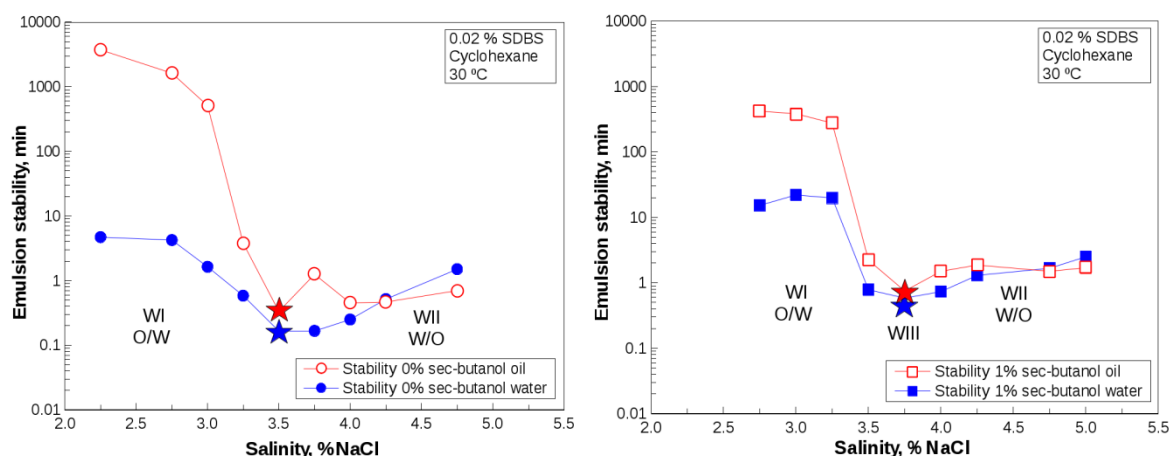


Figure 5. Stability as a function of salinity, with (right) and without (left) alcohol. Surfactant concentration 0.02 wt% alcohol concentration 1 wt%,  $T = 30\text{ }^{\circ}\text{C}$ . Open symbols: time to separate 60% oil, closed symbols: time to separate 60% water. The lines are guides to the eye.

The time needed to separate 60% of oil or water shows a minimum at optimal salinity, as reported in the literature for other low interfacial tension systems (see section *Emulsion stability*). The time corresponding to water resolution is shorter, whatever the emulsion type (excepted at salinities higher than 4.75%); it corresponds to creaming in O/W emulsions and to coalescence in W/O emulsions. In the Winsor III region, the microemulsion separates from both excess oil and water by coalescence. Indeed, the phase separation is too rapid to allow for significant creaming/sedimentation. Whatever the separation criterion, figure 5 clearly corroborate that the emulsion stability is minimum at optimum formulation, as the interfacial properties shown in figure 3. Note that we used logarithmic units in Figure 5, in order to be able to display the lifetimes away from optimum salinity; the minimum is much more visible in linear units. The WII emulsions are less stable than the WI emulsions as in other similar systems<sup>34</sup>, the reason for the dissymmetry being not clear so far.

## Discussion

### Interfacial properties

The area per molecule  $1/\Gamma$  close to the  $C_{\mu c}$  above which the microemulsion phase is present was calculated using the data of figure 4 and the Gibbs equation (equation 8);  $1/\Gamma$  is around  $70\text{ \AA}^2$  in the presence of alcohol and  $60\text{ \AA}^2$  without alcohol. The  $C_{\mu c}$  is 0.027 g/L with no alcohol and 0.019 g/L with alcohol. The  $C_{mc}$  has also been measured in aqueous solutions and found to be somewhat higher, 0.037 g/L with and without alcohol. Note that due to surfactant partitioning between oil and water phases, the surfactant concentration in water at the  $C_{\mu c}$  is smaller than this  $C_{\mu c}$ . It can be seen in figure 4 that when  $\log \gamma$  is plotted versus  $\log C$ , the tension continues to decrease after the  $C_{\mu c}$  before saturating at a higher concentration ( $\sim 0.07\text{ g/L}$ ). This behaviour is not unusual and has been observed with other surfactants in aqueous solutions<sup>79</sup>. Here the interfacial tension is very low at the  $C_{\mu c}$ ; the variations observed beyond are very small and associated to small chemical potential changes, which origin remains to be elucidated.



The interfacial layer is not expected to change significantly in the salinity range explored. Interfacial compression properties have been measured before in these systems, but it has been shown that the elastic bending modulus  $K$  that also reflects the mechanical behaviour of the interfacial layer remains unchanged in similar conditions<sup>80</sup>. The variations of the modulus  $E_{eff}$  are therefore likely due to relaxations. If we assume that these relaxations originate from exchanges between the interface and the bulk phases, we can first think of surfactant monomer exchanges, as described by equations 5-7 of the diffusion model. The interfacial tension data could unfortunately not be used to estimate  $E_{eff}$ , because the interfacial tension remains proportional to  $\ln C$  in the concentration range explored. This is as found with other surfactants, which behave more ideally at oil-water interfaces than at air-water interfaces<sup>66</sup>. We can nevertheless estimate the reduced frequency  $\Omega$  at a frequency 0.1 Hz, using the Langmuir equation 9 to relate  $\Gamma$  and  $C$ : we find  $\Omega \sim 600$  with  $D = 5 \cdot 10^{-10} \text{ m}^2/\text{s}$  and  $a \sim Cmc/20 \sim 0.002 \text{ g/L}$ . The reduced frequency  $\Omega$  is then very large and from equations 5 and 6, one sees that both  $E_{eff}'$  and  $E_{eff}''$  are small and of the order of  $1/(2\Omega)$ . Using  $E \leq 100 \text{ mN/m}$ , we estimate  $E_{eff}' \leq 0.125 \text{ mN/m}$ , a value not far from the measured value of  $0.034 \text{ mN/m}$ . The corresponding relaxation time  $\tau_D$  is small, about 5 ms. However, the model also predicts that the storage and loss moduli should be comparable, while experiments show that the phase angle is quite small and close to zero (figure 4). As the bending modulus  $K$ , the surface concentration does not change with salinity in similar systems<sup>81</sup>. Equations 5 and 9 then predict that the measured elastic modulus  $E_{eff}$  should not change either, unless the Szyszkowski concentration  $a$  changes.

In view of the limited agreement with the diffusion model, in particular for the phase angle  $\phi$ , we can conclude that this model is not appropriate and that the effective modulus is affected by other exchange processes. The exchange times of surfactant between microemulsion structures and oil or water are extremely fast (nanoseconds) as revealed by inelastic neutron scattering<sup>82 83</sup>, too fast to affect the modulus. The decrease of the modulus in the Winsor III region is however certainly linked to the exchanges between oil, water and the interfacial layer. It is known that these exchanges become more rapid close to optimum formulation<sup>84</sup>. A new model accounting for these observations remains to be established.

Let us finally recall that the phase angle  $\phi$  drops to low values above the  $C_{\mu c}$  and remains low in the Winsor III region. Since the middle phase microemulsion does not wet the oil-water interface<sup>85 86 87</sup>, the stretching of microemulsion lenses during the spinning drop elongation might affect the elastic response, even if the amount of microemulsion present is very small. It is however not obvious to evaluate the role of this behaviour on the phase angle  $\phi$ .

## Emulsion stability

It may seem surprising that phase separation due to coalescence and to sedimentation/creaming change with salinity in similar ways. In fact, when coalescence is rapid, the emulsion drop size increases and sedimentation/creaming is also rapid. The literature studies are difficult to compare, because emulsion stability depends on the emulsion drop size, which is determined by the amount of surfactant and the emulsification method used, and largely differs between studies. In a given study, differences can also arise because of changes of interfacial tension (smaller tensions lead to smaller drops<sup>34</sup>), of density difference between phases and of emulsion viscosity, all these changes affecting sedimentation or creaming.

Let us now discuss the question of emulsion stability in light of the models presented earlier. Close to the surfactant concentration for which  $HLD=0$ , the interfacial tension is ultralow and the emulsions are quite unstable as if no surfactant were present at interface, with lifetimes less than minutes<sup>36</sup>. In such a case, the only fast destabilization process is emulsion drop coalescence, creaming/sedimentation or Ostwald ripening being too slow. As explained in the *Background* section, in order for two drops to coalesce, they have to approach and the liquid film between them needs to thin before drop fusion proceeds. The fusion step in moderately stable emulsions is rapid<sup>88</sup>. It occurs via asymmetrical film instabilities, when the film thickness is still large and well before it has reached its equilibrium thickness. These instabilities lead to surfactant depletion at the film surfaces, suppression of the repulsive forces and fast drop coalescence. Their threshold depends on interfacial rheology: the smallest the modulus  $E$ , the easier the instabilities occur<sup>59</sup>. Let us now discuss which modulus needs to be taken into account for film thinning and instability threshold.

When the surfactant is soluble in the drop phase, it can exchange rapidly by diffusion between interface and drops, and replenish film surfaces during film thinning; the modulus to be taken into account is  $E_{eff}$  and the Marangoni force almost vanishes. But when the surfactant is soluble in the emulsion external phase and when the film between two drops is thin enough, there is not enough surfactant to replenish the surfaces and the surfactant has to come back from the film boundaries; this motion takes time, film thinning is controlled by the intrinsic modulus  $E$  and proceeds much more slowly, as if the surfactant were insoluble (figure 1). When the surfactant is partitioned between oil and water, the exchanges between the interface and both oil or water drops are fast because all these drops contain surfactant.

The close relation between stability and elastic modulus found in the experiments performed can thus be rationalized. Table I confirms that the partition coefficients  $k$  are close to one at optimal salinity for the studied systems. Because exchanges are possible between the interface and both oil and water, the modulus playing a role in film thinning is the effective modulus measured at a frequency equal to about the inverse thinning time. Thinning times have recently been measured by Denkov and coworkers for emulsion systems of stability comparable to those investigated here, and found to be of the order of 1-10 s for drops of radius 10-1000 $\mu\text{m}$ <sup>89</sup>. This time scale corresponds well to the frequency of 0.1 Hz used in our measurements. Hence, we are correlating emulsion stability to the interfacial rheology performed at the proper time scale. The threshold for asymmetric film instabilities is low when the effective modulus  $E_{eff}$  is small, leading to unstable emulsions. At optimal salinity,  $E_{eff}$  is extremely small (figure3) and the stability is minimum as expected from the above considerations. Because of surfactant partitioning, all the Marangoni forces are then very small and everything happens as if there were no or very little surfactant at the interface.

Our emulsion experiments use low surfactant concentrations and little microemulsion is present at equilibrium. That might not be the case in practical applications if higher surfactant concentrations are used. Hazlett and Schechter considered that the microemulsion phase could be trapped at the oil-water interface bridging the film and causing instability<sup>37</sup>. However, since the microemulsion does not wet the oil-water interface in the Winsor III region, it is excluded from the interfacial region during film thinning and cannot affect film stability. As shown by Anton and Salager, emulsion stability indeed does not depend on surfactant concentration close to optimal formulation<sup>36</sup>.

Away from the optimal formulation and on the O/W emulsion side, coalescence is less easy and cream emulsions are observed. Here, the surfactant is mainly in the continuous phase, replenishment of film surfaces during thinning is slow and Marangoni forces are important (see figure 1). The hole nucleation models might then become applicable. The curvature energy barrier appears however to be higher than the compression energy barrier far enough from optimal formulation. The hole nucleation is a very fast process, implying that the compression elastic modulus to be considered is the intrinsic modulus  $E$ . In our estimations, we have used a value of 100 mN/m, much larger than the measured effective values shown in Figure 3.

It is also important to stress that in the general case, there could be no correlation between emulsion stability and the modulus  $E_{eff}$  measured at low frequency, because  $E_{eff}$  incorporates surfactant exchange processes that have no time to occur during hole nucleation. This is probably why the correlation between emulsion stability and moduli measured at low frequencies is generally only good with insoluble surface-active species, for which  $E$  and  $E_{eff}$  are close.

## Conclusions

Interfacial rheological properties were measured with a new spinning drop interfacial rheometer, a device that is able to provide accurate data, even for low interfacial tension systems found near the optimum formulation.

The interfacial compression elastic modulus and the phase angle exhibit a minimum at optimum formulation, coinciding with the minimum in interfacial tension and in emulsion stability. The fact that the surfactant is soluble both in oil and water results in fast film thinning, occurrence of axisymmetric instabilities and rapid film rupture, whatever the type of film, oil or water. It is well known that interfacial tension gradients, quantified by the compression modulus  $E$ , usually stabilize one emulsion type (the one with a continuous phase containing the surfactant). Here these gradients are all suppressed because surfactant is always present in emulsion drops. In view of the timescales involved in film thinning, the performed rheological measurements allow the characterization of the actual interfacial tension gradients acting during film thinning. The effective compression modulus is minimum at optimal salinity, explaining why emulsion stability is also minimum.

Going away from optimal salinity, emulsion stability could become progressively controlled by the hole opening mechanism. We propose that emulsion stability is still related to the compression elasticity, but this time to the intrinsic compression modulus which governs the magnitude of the coalescence energy barrier  $W^*$ .

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