DYNAMIC AND RHEOLOGICAL PROPERTIES AT SUPERCRITICAL CO$_2$-WATER INTERFACE.

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ABSTRACT We have measured the dynamical and rheological properties of different surfactants at supercritical CO$_2$-H$_2$O interface by means of a drop tensiometer. It is known that the elasticity of surfactant layers plays an important role in emulsion stability, mainly when it is difficult to achieve electrical and/or sterical repulsion between droplets (this is particularly true in H$_2$O/CO$_2$ emulsion). We first characterized the interfacial tension of pure water-CO$_2$ interface.

In presence of surfactants, the elasticity of the interfacial layer can be written as a sum of two contributions: an equilibrium elasticity (Ee) that describes the molecular interactions in the interfacial layer (i.e. lateral interaction) and a non-equilibrium elasticity (Ene) that can be related to the interactions of surfactant with the adjacent phases (i.e. desorption). Small surfactants like Tween$^®$ or Span$^®$ led to a low elasticity mainly composed of a non-equilibrium part. At contrary, polymeric surfactants like proteins produced interfacial films with an important elasticity. For these systems, Ee and Ene varied with CO$_2$ pressure and with the type of protein.

1   Introduction.

Supercritical carbon dioxide (ScCO$_2$) is becoming increasingly interesting for a lot of application such as medium reaction, non-miscible phase for (micro)emulsion...

A fundamental understanding of interfacial tension (γ), surfactant adsorption and the rheological properties at H$_2$O-CO$_2$ interface is highly useful for designing surfactants necessary in applications involving the H$_2$O-CO$_2$ interface. In ScCO$_2$ systems, only a few studies have measured γ between H$_2$O and CO$_2$ with surfactant [1-3] while no studies included rheology.

Some stable C/W emulsions have been obtained with classical surfactant. At contrary, W/C emulsions coalesce very quickly without use of expensive surfactants containing fluoroalkyl and fluoroether tails [4].

The dispersed droplets in an emulsion are in constant motion and therefore there are frequent collisions between them in absence of steric and/or electrical barrier. In C/W emulsion, this kind of barrier can be created, like this is done in O/W emulsion. Unfortunately, in W/C emulsion it is very difficult to obtain such barrier because:

- Few polymers able to create a steric barrier are soluble in CO$_2$, except fluoropolymers; siloxane and polycarbonate.
- CO$_2$ has a low dielectric constant, which render difficult the creation of a an electrostatic barrier.

Indeed, the mechanical strength of the interfacial film is therefore one of the prime factors determining W/C emulsion stability.

The interfacial elasticity related to the organization of the surfactant layer is such that any applied strain that tend towards local thinning or stretching of the interface is counterbalanced by opposite forces that restore the initial conditions. This elasticity can be separated in two elements:

- An equilibrium elasticity (Ee) which describes surfactant interactions in the interfacial layer (i.e. lateral interaction).
- A non-equilibrium elasticity (Ene) that can be related to the interactions of surfactant with adjacent phases (i.e. desorption) associated with a relaxation time τ representing the necessary time for the interface to reach a new equilibrium energetic state after the perturbation.

A fundamental understanding of interfacial surfactant adsorption, and the rheological properties of W/C interface is then useful for designing surfactants that stabilize efficiently W/C emulsions.

In this present study are measured the interfacial rheological properties of different surfactants at the W/C interface.

2   Materials and Methods

Pendant Drop Tensiometer. The drop tensiometer (Tracker, IT Concept, France) allows the determination of the interfacial tension by analyzing the axial symmetric shape (Laplacian profile) of the pendant drop (aqueous phase) in CO_2. The apparatus consisted of a view cells under CO_2 atmosphere, a light source, a CCD camera, a computer, a syringe and a motor.
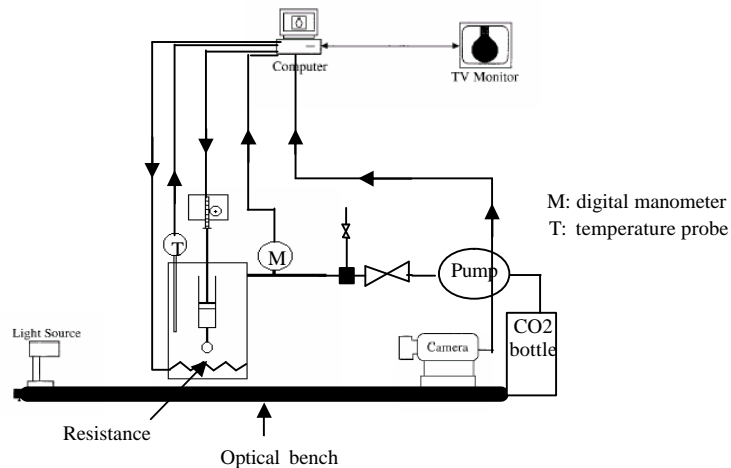
Figure 1: Dynamic drop tensiometer

Pendant drops were formed at the end of a stainless steel tube with an inside diameter of 1 mm, connect at a syringe whose the **area is controlled during all the time of experience by the motor**. The interfacial tension is determined by first digitising and analysing the profile of the droplet using a CCD camera coupled to a video image profile digitiser board connect to a computer [5].

Rheological measurements.

The common idea of all the related rheological experiments is to apply a controlled perturbation to the surface in order to simultaneously follow the related surface pressure variations.

The dynamic response of a surface film to a dilatational mechanical stress in the time scale of 1-10^3 s is studied by means of two experimental approaches.

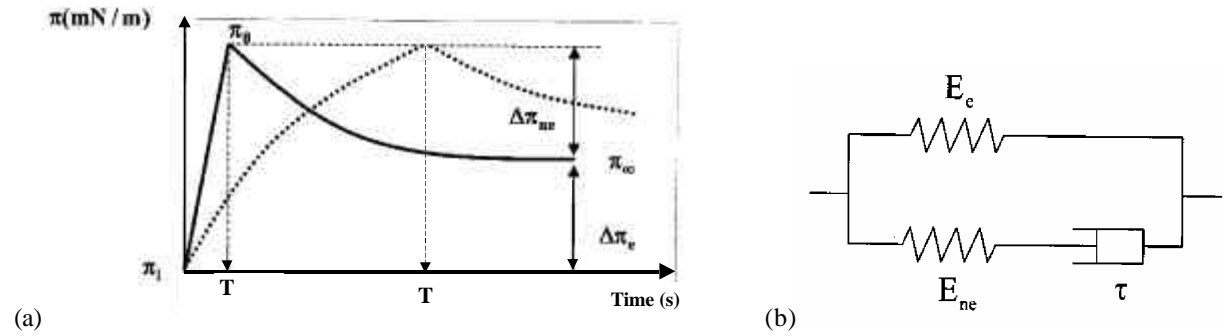**Ramp Type Perturbation Approach.**

The first approach consists of a continuous and monotonic compression of a surface layer on a pendant drop after the application of small disturbances (Figure 2).

In this case, a convenient theoretical model, corresponding to a solid viscoelastic body, has been developed and applied to many kinds of interfacial systems (phospholipids or polymers) [6-9] .

We obtained the following equation to describe the viscoelastic behaviour of the monolayer.

$$\frac{\Delta\Pi}{U_b t} Ai = E_e + E_{ne} \frac{t}{t}\left(1 - e^{-t/t}\right) \qquad \text{(Eq 1)}$$

Using the experimental values found for $\Delta\Pi$ (t) along with eq 1, it is possible to determine the nonequilibrium part (E_{ne}) and the equilibrium part (E_e) of the dilatational elasticity. The specific time of relaxation τ could be easily determined from experiments of relaxation.

Figure 2: (a) Surface pressure change $\Delta\Pi$ during the time T. (bold line: fast compression; thin line: slow compression). (b) mechanical model

Sinusoidal Perturbation Approach.

The second approach seems very close to the common 3D rheology field. A sinusoidal interfacial deformation is applied in order to follow the interfacial tension response. Relative area variation and surface tension are considered, respectively, as the input and the output of the interfacial system, from which it is possible to evaluate a transfer function (complex function) often called complex elasticity modulus E. The real part of this function characterizes a conservative monolayer comportment. The imaginary part characterizes a dissipative monolayer comportment [5].

3   Results and Discussion.

3.1   Water-CO$_2$ interface.

The interfacial tension between pure CO_2 and water is shown in Figure 3 for a temperature of 40°C as a function of pressure.
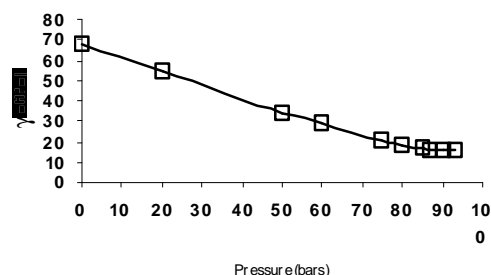
Figure 3: Variation of equilibrium water-CO_2 interfacial tension versus CO_2 pressure.

These results are in accordance with previous experiments done by other groups and allowed us to validate our experimental set up. [1-3]

3.2   Interfacial properties of adsorbed layer.

Human Serum Albumin (HSA).

We present in figure 4 the variation of γ versus time in presence of 0.84 g/L of HSA, at different pressures. The obtained curves showed three steps to reach an equilibrium value, characterized by times of 40, 400 and 6000 seconds. These can be interpreted as a rapid adsorption of protein segments at the interface followed by a rearrangement of the adsorbed film that is frequently observed at water/oil interfaces [10].
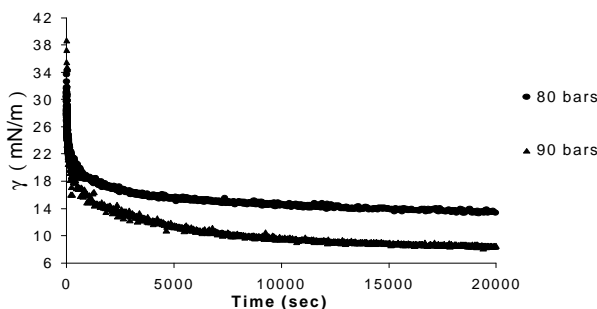
Figure 4: Kinetics of HSA adsorption at water-CO_2 interface.

The rheological parameters have been determined in function of CO_2 pressure by the two approaches described above and similar results were obtained in both cases (figure 5). The comparison of both parameters Ee and Ene indicated that the organisation of the protein at the interface was influenced by the pressure and therefore by the density and polarity of CO_2. Ee reflects the density of segments anchored at the interface and their ability to stay in this conformation. In that way, Ee describes the lateral interaction between the protein and the segment of protein in interfacial zone. Ene characterizes the dissipation of the rheological perturbation energy related to interactions between the interfacial protein segment and bulk phases. These interactions occurs by the desorption of segments through the interface as loop-shape. One can see that Ee reached a maximum value near 80 bars, while Ene reach a minimum. These results indicates that at a this peculiar pressure the protein is strongly anchored at the interface and less interact with the adjacent phases.

Below this pressure the dissipative characters of the interfacial layer is related to the expulsion of segments towards the aqueous phase. At contrary we can assume that after 80 bars, the expulsion of protein segments is oriented towards the CO_2 phase which is became a better solvent for protein segments.

a   b
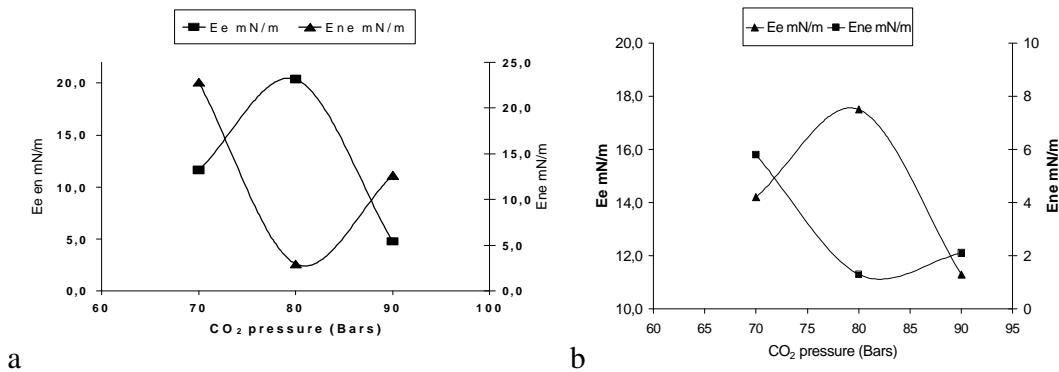
**Figure 5: HSA rheology (a) Ramp type rheology (b) Sinusoidal type rheology**

Surfactant: Tween® 20 and Span® 20.

The adsorption kinetics of Tween and Span 20 at a concentration of 1g/L are shown in Figure 6. Equilibrium values were very quickly reached for both molecules. Tween adsorption occurred in three steps, while Span adsorption involved two steps. We remarked that Tween 20 molecules were little more active at interfaces than Span 20. These molecules have the same nonpolar part, but the polar part of Tween is more important than in Span molecules. So, one can thinks that a some compromise between the polar and nonpolar part of a surfactant is necessary to have a good affinity for H_2O-CO_2 interface.

The rheological parameters of Span determined by the two methods showed that the values of elasticity were lower than the value obtained with HSA. These values, mainly composed of a non-equilibrium elasticity part, showed that Span molecules were few anchored at the H_2O-CO_2 interface. Ee and Ene showed a minimum near 70 bars. The increase of Ee with the CO_2 pressure indicated an increase of lateral interaction with the CO_2 pressure.

CONCLUSION

We demonstrated that interfacial layers formed from classical and macromolecular amphiphiles were able to be analysed by means of a pendant drop technique at the CO_2/water interface. This technique allowed us to study the kinetics aspects of the adsorption and also to precisely measure the dilatational properties of the films. These approached is promising for better understand the phenomena that occur in the emulsion-based processes and shown that a polymeric molecule could created a more cohesive film at the H_2O-CO_2 interface than little surfactant. Indeed macromolecules may be useful to inhibit the coalescence of water drop in a CO_2 surrounding media.
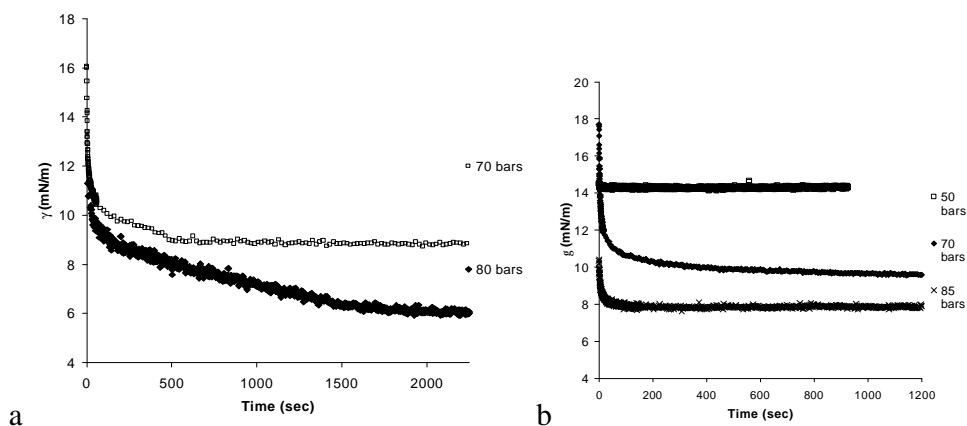
Figure 6: kinetics of adsorption at water-CO_2 interface at 40°C (a) Tween 20 (b) Span 20

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