

# MEASUREMENTS OF INTERFACIAL TENSION AND INVESTIGATION OF LIQUID DISPERSION IN SUPERCRITICAL MEDIA

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## ABSTRACT

Interfacial tensions at the interfaces: water/CO<sub>2</sub>, ethyl alcohol/CO<sub>2</sub> and methylene chloride/CO<sub>2</sub> were measured versus pressure at 308 K and using the pendant drop method. Interfacial tension at the interface water/ CO<sub>2</sub> decreases linearly when pressure increases from 0.1 to 9 MPa and remains constant with a pressure ranging from 10 to 15 MPa. These results are conform to literature data. Interfacial tensions at the interfaces: ethyl alcohol/CO<sub>2</sub> and methylene chloride/CO<sub>2</sub> decrease in the same order of magnitude when pressure increases from 0.1 to 8 MPa. The values of interfacial tension measured at 8 MPa and 308 K were used to estimate the regime and modes of dispersion for water, ethyl alcohol and methylene chloride into supercritical CO<sub>2</sub> in a certain range of flow rates corresponding to those commonly used in SAS process applications. Direct visualization of liquid dispersion into supercritical carbon dioxide in the same experimental conditions proved that the estimates were relevant.

## INTRODUCTION

The hydrodynamics of a liquid phase dispersion into a supercritical one is not well understood, though it is a determining step in the Supercritical Anti-Solvent (SAS) precipitation process. Indeed, the size and morphology of the particles obtained by SAS process are related to the precipitation vessel hydrodynamics' conditions [1]. A first advance would be the prediction of the liquid phase dispersion mode during the SAS process for given experimental conditions. But for such an approach, some fundamental data like interfacial tension have to be known.

The objective of this study is to measure interfacial tension at the interface between a liquid phase and carbon dioxide and to use the data measurement to predict the regime and modes of dispersion of the liquid phase during SAS process.

The solvents commonly used in SAS process are miscible with CO<sub>2</sub> within the whole experimental range of pressure and temperature conditions, so the interfacial tension at the organic solvent-CO<sub>2</sub> interface is dynamic. The composition of each phase (the dispersed and the continuous one) evolves during the dispersion. There is rather little studies in literature dealing with dynamic interfacial tension measurements at interfaces involving carbon dioxide. Some works related the measurements of interfacial tension at the interface water-CO<sub>2</sub>, using the capillary rise technique [2] or the pendant drop method [3, 4]. Interfacial tension of ethyl alcohol in contact with CO<sub>2</sub> have been recently measured by laser interferometric microscopy

[5]. Since water is far from being soluble in CO<sub>2</sub>, the measurement can be made at the equilibrium.

This work comprises two parts. In the first part, the interfacial tensions versus pressure at the interfaces: water/CO<sub>2</sub>, ethyl alcohol/CO<sub>2</sub> and methylene chloride/CO<sub>2</sub> are measured at 308 K. The measurements concerning water are compared to literature data [2, 3, 4]. The data measurements of interfacial tension at 8 MPa and 308 K were used to predict the modes of dispersion of water, methylene chloride and ethyl alcohol into supercritical carbon dioxide (SC CO<sub>2</sub>) as a function of liquid flow rate. In parallel, the different regimes and modes of dispersion into SC CO<sub>2</sub> are investigated by direct visualisation. The objective of such an approach is to be able to predict the experimental conditions leading to an atomized jet during SAS processes.

## I. THEORY AND EXPERIMENTAL METHODS

### I. 1. INTERFACIAL TENSION MEASUREMENTS - HANGING DROP METHOD

A drop of controlled volume of water is formed through a stainless steel needle. If the arrangement is vertical, a hanging drop is obtained, the shape of which is controlled by the balance between interfacial tension and buoyancy. The interfacial tension tends to make the drop spherical whereas the gravity tends to elongate it. Optical measurements of a drop profile allow measuring the interfacial tension,  $\gamma$ , with good accuracy if the buoyancy forces are non negligible (more than 1%) as compared to the capillary forces. This is achieved with large enough drop volumes. Knowledge of the densities to third digit is also necessary. The interfacial tension is determined using the Laplace's equation which relates the local radii of curvature  $R$  and  $R'$  at point  $M$  (see figure 1) to the pressure difference  $\Delta P$  between the inner and outer media. The coefficient of proportionality yields directly the interfacial tension  $\gamma$  :

$$\Delta P = \gamma \left( \frac{1}{R} + \frac{1}{R'} \right) \quad (1)$$

The equation which expresses the equilibrium of the forces across the horizontal plane passing by  $M$  can be used to relate the drop volume  $V$  beneath the plane to  $\Delta p$  :

$$2 \pi x \gamma \sin \theta = V \Delta \rho g z + \pi x^2 \Delta p \quad (2)$$

where :  
 $x$  and  $z$  are the coordinates of  $M$  ( $z=0$  corresponds to the apex of the drop),  
 $\theta$  is the polar angle of the tangent to  $M$  with the  $Ox$  axis,  
 $\Delta \rho$  is the specific density difference between the two fluids.

The drop is created in a pressure chamber (see figure 2) and is illuminated by a diffuse light source, the projection of its profile is monitored optically on a CCD camera connected to a dedicated computer for fast image analysis (25 images per second).

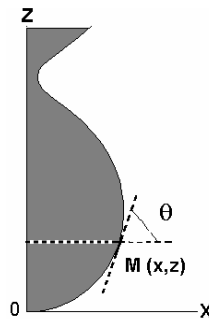


Fig. 1: Typical profile of the hanging drop (assuming cylindrical symmetry around the vertical axis).

The same procedure is followed for methylene chloride and ethyl alcohol using a teflon tip at the outlet of the needle. For both solvents, the droplet volume and shape evolve

rapidly because of the mass transfer of carbon dioxide into the liquid droplet and of the solvent towards the continuous phase. In that case, the image of the first biggest pendant drop is used to estimate the interfacial tension.

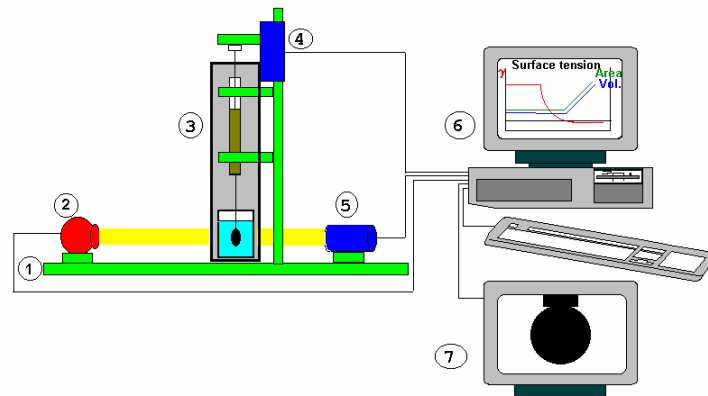


Fig. 2 : Schematic of the drop tensiometer : Table (1), light source (2), pressure chamber (3), computer-controlled dc motor drive for the syringe piston (4), CCD camera (5), micro computer (6), video monitor(7).

## I. 2. DISPERSION

When a liquid phase is dispersed through a capillary, three principal regimes may be observed [6]:

- "Dripping" regime: the droplets are formed at the orifice of the capillary,
- Laminar regime: the jet has a smooth and continuous aspect at the outlet of the capillary and at the breakup, there is a quasi-periodic emission of droplets identical in size,
- Turbulent regime : the jet surface presents irregularities and the droplets formed have different sizes.

During the dispersion, the velocity of the liquid phase is one of the key parameters that determine the hydrodynamics state and the instability of the jet.

In laminar flow, the appearance of these different unstable modes of jet is controlled by several competing effects: capillar, inertial, viscous and aerodynamic effects between the jet surface and the continuous phase. A characteristic time is associated with each effect :  $t_{cap} = (\rho_l D^3 / \gamma)^{0.5}$ ,  $t_{in} = (D / U_o)$ ,  $t_{vis} = (D^2 / \nu_l)$ ,  $t_{aer} = (\rho_l D^2 / \rho_{CO2} U_o^2)^{0.5}$ ,  $t_{gr} = (U_o / g)$ . Gravity effects can be ignored when the characteristic time associated with this effect is much higher than the one associated with the inertial effects ( $Fr_1 \gg 1$ ).

The dominating effects show the shortest characteristic times. When the capillar effects are dominating, the jet breakup length (distance between the outlet of the capillary and the points where the droplets are formed) increases versus flow rate while the decreasing of the breakup length versus flow rate is attributed to the combination of inertial, viscous and aerodynamic effects. Therefore, the calculation of these different characteristic times makes it possible to predict the value of flow rate for which aerodynamic effects are dominating leading the decreasing of breakup length versus flow rate corresponding to an asymmetric laminar jet. When the decrease of the characteristic time associated to the aerodynamic effect versus flow rate is much less marked, the jet is generally atomized at the outlet of the capillary.

The experimental device used for the acquisition of dispersion video is detailed elsewhere [1]. In order to make direct measurements, the vessel is different than usual vessels used for precipitation processes and it is equipped with two thick facing borosilicate windows. It has been manufactured by New Ways of Analytics (Germany). The total volume of the high pressure vessel is 763 mL. The temperature of the vessel is kept constant with an automatic regulation system comprising a thermocouple and an electric heating system.

For the acquisition, an analogic video camera is used, focused on the exit of the capillary. The camera is connected to a PC in order to acquire the videos using an interface card and a software (Pinnacle Studio).

## II. RESULTS AND DISCUSSION

### II. 1. INTERFACIAL TENSION

Figure 3a shows the variation versus pressure of the interfacial tension at the interface between a water droplet in contact with pure carbon dioxide. At pressures below 9 MPa, the interfacial tension decreases when the pressure increases. Above 9 MPa, the interfacial tension remains quite constant. These results are comparable to the ones obtained by other authors. A cusp in the curve appears around 9 MPa, this has already been observed and discussed by Da Rocha and coll. [3]. A typical profile for water droplet at 308 K and 10 MPa is shown in figure 4.

Figure 3b shows dynamic interfacial tension at the interface between an ethyl alcohol or a methylene chloride droplet in contact with pure carbon dioxide versus pressure. The interfacial tension fall is quite pronounced over the pressure range studied and is in the same order of magnitude for both solvents. Above 8 MPa, the measurements were not realizable because of too much rapid mass transfers.

The characteristic times associated to the capillary, the aerodynamic and inertial effects were calculated. Figure 5 shows the variation of these characteristic times versus flow rate for water dispersion at 308 K and 8 MPa. In these conditions of temperature and pressure, the interfacial tension value used for these calculations is  $27.5 \cdot 10^{-3} \text{ N}\cdot\text{m}^{-1}$ , which corresponds to the measurements described above. For water, in the studied range of flow rates, we observed that for the very low flow rates, the characteristic time associated to the capillary effect is the shortest while for higher flow rates, the characteristic times associated to the aerodynamic and the inertial effects become the shortest and do not vary any more above  $200 \text{ mL}\cdot\text{h}^{-1}$ .

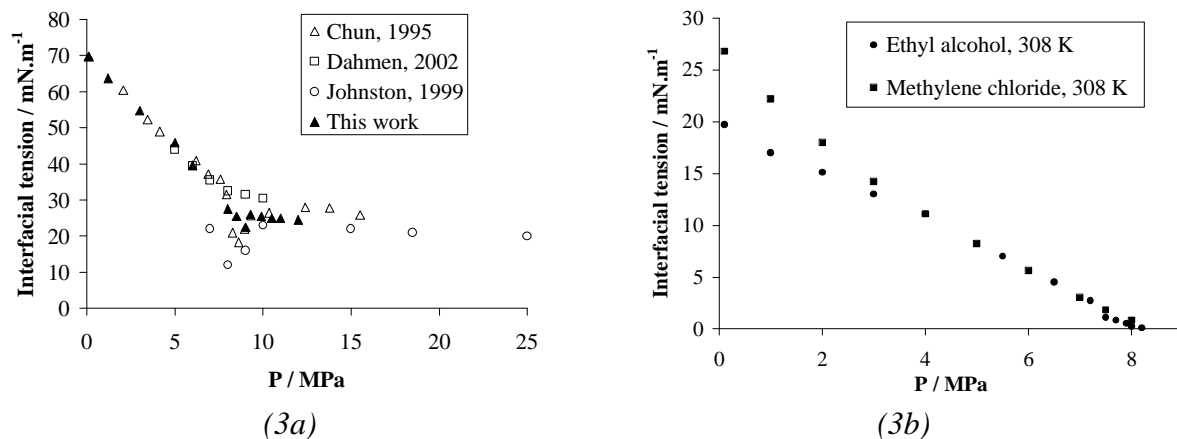


Fig. 3: Interfacial tension at the CO<sub>2</sub>-water interface (3a) and at the CO<sub>2</sub>-solvent interface (3b) versus pressure at 308 K.



Fig. 4: Drop of water in supercritical  $\text{CO}_2$  (10 MPa, 308 K)

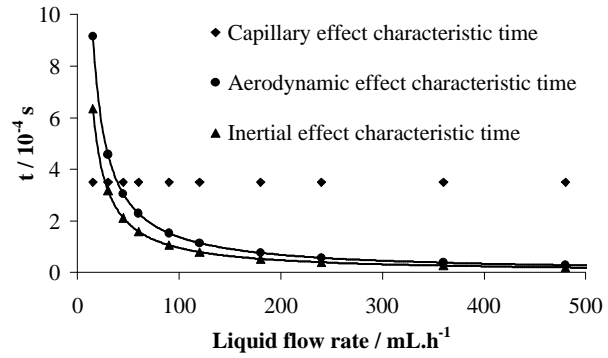


Fig. 5: Characteristic times (calculated at 308 K and 8 MPa) versus flow rate for water.

Results obtained for methylene chloride are identical to those for ethyl alcohol, but in that cases, the time associated to the capillary effect is always higher than the times associated to the aerodynamic and inertial effects. Figure 6 shows the variation of the characteristic times associated to these latter effects versus flow rate at 308 K and 8 MPa. The characteristic times associated to the capillary effects are about 3.2 ms for ethyl alcohol and about 2.3 ms for methylene chloride. The calculations have been made using the physico-chemical properties of each fluid at 308 K and 8 MPa. The interfacial tension value used for methylene chloride is  $0.8 \cdot 10^{-3}$  and  $0.25 \cdot 10^{-3} \text{ N.m}^{-1}$  for ethyl alcohol, values corresponding to the measurements described above.

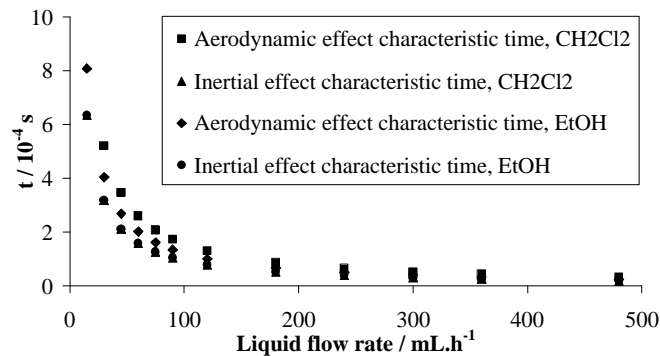


Fig. 6: Characteristic times (calculated at 308 K and 8 MPa) versus flow rate for methylene chloride and ethyl alcohol.

## II. 2. DISPERSION

The dispersions of water, ethyl alcohol and methylene chloride into a SC  $\text{CO}_2$  continuous phase were visualized for a liquid flow rate varying from 15 to 300  $\text{mL.h}^{-1}$ . Figure 7 shows the dispersion of methylene chloride (7a-7d) and of water (7e-7h) into SC  $\text{CO}_2$  at 308 K and 8 MPa. In both cases, for the first three photos, the dispersed liquid phases form a laminar asymmetric helicoidal jet. Indeed, the breakup decreases when the flow rate increases, which is characteristic of an asymmetric jet. Within the range of flow rate investigated, we observed for the three liquids of interest, the transition between a dispersion by formation of a plain laminar jet and the dispersion by jet atomization. In the only case of water, a drop by drop dispersion was observed for the lowest flow rates. Still for water, a plain laminar jet dispersion started from  $75 \text{ mL.h}^{-1}$  and the transition between a plain laminar jet and an atomized jet was observed at  $270 \text{ mL.h}^{-1}$ . It is interesting to note that this range of flow rate ( $75$  to  $270 \text{ mL.h}^{-1}$ ) corresponds to the domain of flow rate for which the aerodynamic effect is one of the dominating effects and for which its characteristic time associated decreases. The

jet is atomized for higher flow rates corresponding to the domain of very slight decrease of the time associated to this effect (see figure 5).

The transition between a plain laminar jet and an atomized jet was observed at 60 mL.h<sup>-1</sup> for ethyl alcohol and at 30 mL.h<sup>-1</sup> for methylene chloride. For both solvents, the jet is atomized when the decrease of the characteristic time associated to the aerodynamic effect is much less marked (see figure 6).

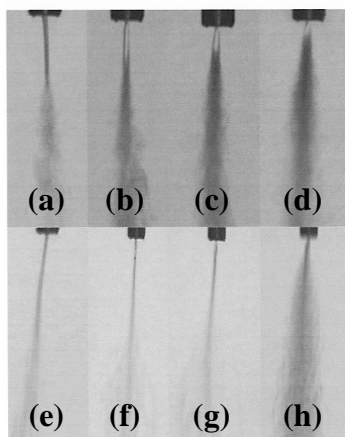


Fig. 7: Dispersion of methylene chloride ((a): 3; (b): 6; (c): 21; (d): 30 mL.h<sup>-1</sup>) and of water((e): 75; (f): 120; (g): 240; (h): 285 mL.h<sup>-1</sup>) in SC CO<sub>2</sub> at 308 K and 8 MPa.

## CONCLUSION

The approach presented in this work allows to predict the formation of a plain asymmetric jet or the formation of an atomized jet. In the case of polymeric precipitation, the formation of fibers instead of microparticles has already been observed [1] and it was proved that the formation of fibers was due to the formation of a plain jet during the liquid dispersion. So, since the interfacial tension is known, the mode of dispersion of the liquid phase can be predicted. As seen above, within the range of this study, various dispersion modes are involved depending on the liquid flow rate. This range of flow rate corresponds to the ones commonly used for SAS process applications. Thus, the knowledge of the dispersion mode is of great interest for controlling powder characteristics.

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## NOTATION:

D: Capillary internal diameter (m); Q<sub>l</sub>: Feed flow rate of liquid phase (mL.h<sup>-1</sup>); ν<sub>l</sub>: Kinematic viscosity of liquid phase (m<sup>2</sup>.s<sup>-1</sup>); ρ<sub>l</sub>: Density of liquid solution (kg.m<sup>-3</sup>); ρ<sub>CO<sub>2</sub></sub>: Density of carbon dioxide (kg.m<sup>-3</sup>); γ: Interfacial tension of liquid phase in contact with supercritical phase (N.m<sup>-1</sup>); U<sub>o</sub>: Velocity of liquid phase (m.s<sup>-1</sup>); g: Gravity constant (m.s<sup>-2</sup>); Fr<sub>l</sub>: Froude number characterising the liquid phase flow.