



# Interfacial tension of marine lipids in contact with high pressure carbon dioxide

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## ABSTRACT

Interfacial tension (IFT) of fish oil triglycerides (TG) and fatty acid ethyl esters (FAEE) in contact with carbon dioxide (CO<sub>2</sub>) was measured according to the pendant drop method at 40, 55 and 70 °C and pressures up to 25 MPa. The IFT of both TG and FAEE decreased substantially with CO<sub>2</sub> pressure. The IFT of FAEE vanished at elevated pressures, whereas that of TG decreased to a fairly constant level of about 2 mN/m. The IFT was correlated using a model taking into account the density, pressure and temperature of CO<sub>2</sub>, thereby facilitating the calculation of the ideal pendant drop volume as well as the surface excess concentration of CO<sub>2</sub>. In the pressure range studied, the pendant drop volume for FAEE decreased with pressure, whereas for TG it increased at elevated pressures due to the predominant effect of buoyancy. Furthermore, the change in IFT over time was determined at 55 °C for TG in contact with CO<sub>2</sub> at pressures up to 11.4 MPa showing a decrease of IFT over time at low pressures, whereas at higher pressures it remained nearly constant. IFT influences drop formation as well as the disintegration of falling films thereby affecting the performance of separation processes.

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## 1. Introduction

Interfacial phenomena play an important role in high pressure processes involving liquid/liquid or gas/liquid systems, where the interface between immiscible phases influences mass transfer, heat transfer and hydrodynamic flow regimes. Interfacial tension (IFT) is an important parameter to characterize the interface. IFT is correlated to the amount of energy required to increase interfacial area, which is important in many unit operations and a key parameter for drop formation, spray jet break-up as well as falling film stability. The IFT is largely affected by pressure in high pressure systems with a considerable solubility of the dense gas in the liquid. Therefore, IFT has major implications for the design of processes involving lipids and supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>). It has been observed that a falling film of fatty acids in contact with SC-CO<sub>2</sub> disintegrates into a swarm of fine droplets once a certain pressure is exceeded, even under flow regimes with very little mechanical energy input [1]. IFT in those systems was identified to be one of the reasons for that film disintegration [2]. However, it was shown later that fluid dynamics (liquid film velocity) and physicochemical effects (IFT, viscosity) in combination are the cause of film disintegration [3]. Nevertheless, IFT is a key parameter to characterize the boundaries for different flow regimes of a falling film as well as jet break-up.

Moser and Trepp [3] studied falling films of squalene and  $\alpha$ -tocopherol in high pressure CO<sub>2</sub> at various liquid flow rates. They

found that the transition from a stable film to disintegration into droplets can be characterized by the dimensionless Weber number ( $We$ ), Reynolds number ( $Re$ ) and film number ( $K_F$ ) [3]. IFT is required for the calculation of  $We$  and  $K_F$ . Besides IFT, viscosity is an important factor in the film disintegration as well, which is also influenced by the increasing solubility of CO<sub>2</sub> in lipids with pressure [4]. Flow regimes of falling films and break-up of free jets in the binary system methyl myristate + CO<sub>2</sub> were studied by Kerst et al. [5] using a high pressure view cell and photo imaging. They developed correlations based on dimensionless numbers such as  $Re$ ,  $K_F$  and Ohnesorge number ( $Oh$ ), to characterize the flow regime of falling films and the jet disintegration length [5], where IFT is again required for calculating  $Oh$ . Stockfleth and Brunner [6] investigated film thickness, flow regimes, and flooding points for the countercurrent annular flow of corn oil and CO<sub>2</sub> at 65 °C and pressures of up to 20.6 MPa using an experimental setup, which allowed varying both the liquid and gas flow rates. The break-up of the falling film was influenced by the countercurrent gas flow rate leading to increased shear forces, thereby shifting the transition between the flow regimes (crest and drop formation) to lower  $Re$  for the liquid film. A newly introduced gas resistance factor was used to calculate a modified  $Re$ , which was then plotted versus  $K_F$ , thereby facilitating the prediction of the transition zones between flow regimes in situations with a countercurrent gas flow. Jet break-up in a high pressure environment was studied by Czerwonatis and Eggers [7], who developed a correlation based on a new dimensionless number, which requires IFT, to characterize the transition between regimes of jet disintegration, such as Rayleigh break-up, sinuous wave break-up and atomization. Furthermore, Badens et

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al. [8] studied the jet formation and break-up of water, methylene chloride and ethyl alcohol into pressurized CO<sub>2</sub>, and developed a new correlation between  $Oh$  and the jet  $Re$  to determine the transition to the atomization regime, which required the knowledge of IFT. Sutjiadi-Sia and Eggers [9] studied the lateral wetting angle of falling films consisting of water in dense CO<sub>2</sub>, and found that the wettability on a horizontal glass or stainless steel surface decreased with increasing pressure. The IFT between each of the three adjacent phases (solid, liquid, vapor) influences the wettability and thus the contact angle between the solid surface and the liquid falling film [10].

IFT of lipids in contact with CO<sub>2</sub> has been investigated in numerous studies. Schiemann and co-workers [11,12] determined the IFT of several lipids (pelargonic acid, stearic acid, oleic acid, monoglycerides, and vegetable oils) in contact with various gases, including CO<sub>2</sub>, ethane, nitrogen, argon, helium, and hydrogen applying the pendant drop method, the capillary rise method and the du Noüy ring method using a high pressure view cell. In most systems investigated the gas was soluble in the non-volatile liquid phase, which caused a decrease in IFT with increasing pressure. However, for the binary system pelargonic acid + helium the IFT increased with pressure [11,12]. Such pressure induced increase of IFT in systems where the gas exhibits a very low solubility in the non-volatile phase had been suggested by Rice [13]. However, in most systems the gases exhibit an appreciable solubility in the liquid phase and therefore this pressure effect has been overcome and not observed. The pendant drop method to determine IFT has been employed for other binary CO<sub>2</sub> + lipid systems, which include olive oil [14], corn germ oil [15], wheat germ oil and palm oil [16]. Furthermore, Lockemann [17] determined the IFT of binary CO<sub>2</sub> + lipid systems including oleic acid, methyl myristate, methyl palmitate as well as the ternary system CO<sub>2</sub> + methyl myristate + methyl palmitate using the capillary rise method.

Literature is lacking IFT data for marine lipids in contact with high pressure CO<sub>2</sub>. Therefore, the objectives of this study were to determine the IFT of marine lipids in the form of TG and FAEE in contact with high pressure CO<sub>2</sub> and to develop a correlation to describe the data. An apparatus for measuring IFT of liquids under high pressure based on the pendant drop method was designed and built for this purpose. Using the correlation for IFT, the ideal pendant drop volume was calculated according to Tate's law by balancing interfacial, buoyant and gravitational forces. Furthermore, this study aimed to elucidate the change in IFT of TG over time in high pressure CO<sub>2</sub>. Additionally, the surface excess of CO<sub>2</sub> was assessed by using the correlation derived for the IFT data in this study.

## 2. Experimental

### 2.1. Theory of pendant drop method and prerequisites

To determine the IFT for high pressure systems the pendant drop method introduced in 1938 by Andreas et al. [18] seems to be the most reliable method up to date. The contour of a pendant drop suspended from a capillary needle depends on the capillary diameter, IFT and density difference between the drop and surrounding fluid. A balance between gravitational, buoyant and interfacial forces acting on the interface of a drop of liquid suspended in another immiscible fluid leads to the Young–Laplace equation [19,20]:

$$\gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2\gamma}{R} - \Delta\rho g z \quad (1)$$

where  $\gamma$  is the interfacial tension,  $R$  the radius of curvature in the apex,  $\Delta\rho$  the density difference between drop forming liquid and the surrounding fluid,  $g$  the acceleration due to gravity and  $z$  the distance from the apex. As illustrated in Fig. 1,  $R_1$  and  $R_2$  are the

principal radii of the drop interface at distance  $z$  from the apex, with  $R_1$  being the radius of curvature in the plane of Fig. 1 and  $R_2$  the radius of curvature in a plane perpendicular to Fig. 1. In case of an axisymmetric system, which is the case for a pendant drop, the following geometrical relationships are used to substitute  $R_1$  and  $R_2$  in Eq. (1)

$$R_1 = \frac{\left[ 1 + \left( \frac{dz}{dx} \right)^2 \right]^{3/2}}{d^2z/dx^2} \quad (2)$$

$$R_2 = \frac{x}{\sin(\Phi)} \quad (3)$$

with

$$\sin(\Phi) = \frac{dz/dx}{\left[ \left( 1 + dz/dx \right)^2 \right]^{1/2}} \quad (4)$$

Hence, a non-linear differential equation of second order is derived, which was solved numerically by Bashford and Adams in 1883 for sessile drops [21]. Since then numerical algorithms have been implemented in software capable of performing axisymmetrical drop shape analysis (ADSA) by numerically integrating the differential equation describing the drop profile of the pendant drop [22].

In order to evaluate the IFT based on the image of a pendant drop the densities of both the liquid forming the drop as well as the surrounding fluid are required. In high pressure systems, especially those where the surrounding fluid is highly soluble in the liquid phase the liquid density may increase (lipid + CO<sub>2</sub>) [23] or decrease (lipid + propane or ethane) [11] with pressure and needs to be known prior to IFT measurements.

### 2.2. Materials

Corn oil (Mazola®) was purchased at a local store and used without further treatment for IFT measurements. Refined fish oil extracted from anchovy and sardine was obtained from Ocean Nutrition Canada (ONC, Halifax, NS, Canada) in the form of triglycerides (TG) and fatty acid ethyl esters (FAEE) for the IFT measurements. The fatty acid profiles as provided by the manufacturer for the fish oil in the form of TG (ONC product code: XOTDHA-NG) stated a level of 8% and 25%, whereas that for the FAEE (ONC product code: XO4020EE) was 42% and 21% for EPA and DHA, respectively. Further specifications for both oils were provided previously [23]. As stated by the manufacturer, the oils contain about 8 mg/g of antioxidants, including a mix of natural tocopherols and citric acid. Both TG and FAEE were used without further treatment and stored at 4 °C in aluminum bottles with nitrogen filled headspace to minimize any degradation. Food grade anhydrous ethanol (Commercial Alcohol, Winnipeg, MB, Canada) was used for cleaning and IFT measurements. Bone dry CO<sub>2</sub> with a purity of 99.9% (Praxair, Edmonton, AB, Canada) was used for the IFT measurements. Nitrogen with a purity of 99.998% (Praxair, Edmonton, AB, Canada) was used to fill the headspace of the aluminum bottles containing the fish oil after each opening.

### 2.3. IFT measurements

#### 2.3.1. Apparatus to determine IFT

The apparatus to determine the IFT under high pressure conditions according to the pendant drop method consisted of a 200 mL high pressure view cell with an internal diameter of 40 mm (Nova-Swiss, Effretikon, Switzerland) equipped with electric heaters and placed in a temperature controlled insulated air bath (Fig. 2). The temperatures of both the air bath and electric heaters were individually controlled by means of J-type thermocouples connected to

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