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Dynamic and rheological properties of classic and macromolecular surfactant at the supercritical CO_2–H_2O interface

Frederic Tewes, Frank Boury *

Inserm U646, Ingénierie de la Vectorisation Particulaire, Université d'Angers, Bat. IBT,
10 rue A. Boquel, Angers F-49100, France

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Abstract

For the first time, rheological and dynamical properties of various interfacial layers separating an aqueous phase and a carbon dioxide phase under supercritical conditions have been measured by means of a drop tensiometer, applying either sinusoidal or ramp interfacial area perturbation. Those approaches have been largely developed on liquid–air and liquid–liquid interface but very few studies were performed in pressurized conditions [F. Tewes, F. Boury, Formation and rheological properties of the supercritical CO_2–water pure interface, J. Phys. Chem. B 109 (2005) 3990–3997; F. Tewes, F. Boury, Effect of H_2O–CO_2 organization on ovalbumin adsorption at the supercritical CO_2–water interface, J. Phys. Chem. B 109 (2005) 1874–1881].

For small surfactants, such as Tween® molecules, same results for equilibrium elasticity (E_e) values were obtained whatever the perturbation mode. However, non-equilibrium elasticity values (E_{ne}) were in some cases significantly influenced by the kind of perturbation. Rheological measurements evidenced the effect of the size of the alkyl tail upon the rheological properties of the interface. In particular, an alkyl chain composed of 16 carbon atoms facilitated the formation of a mixed interface constituted from Tween® molecules and a network of structured H_2O–CO_2 molecules.

Polymeric molecules like human serum albumin (HSA), produced interfacial films with an important elasticity. For these systems, E_e and E_{ne} varied with CO_2 pressure and with the type of protein.

Keywords: Interfacial tension; Supercritical; Protein; Surfactants; Adsorption; Dilational rheology

1. Introduction

The interest in the use of carbon dioxide into supercritical conditions ($ScCO_2$) increases for a lot of application such as medium reaction [3], foaming agent or non-miscible phase for emulsion and microemulsion formulation [4]. This can be attributed to the peculiar physical properties of supercritical fluids, allowing easily and in continuous way the tuning of their density and their solvent power. Moreover, the use of CO_2 answers to the need of the substituting toxic and environmentally bad organic solvent in the industrial processes.

In the last years, many studies deal with the formation of W/C and C/W microemulsion [4–6] and emulsion [7]. The first experiments were feasibility studies, with the search of very CO_2-soluble surfactant (i.e. with fluoroalkyl, fluoroether or silicone tails). Almost studies were based on phase behavior, droplet size determination, solubilization efficiency, conductivity and interfacial tension measurements [7–11]. However, a small number of studies have measured γ between H_2O and CO_2 in presence of surfactant [2,7,11–15] and few of these studies included interfacial rheology measurement [2].

The dispersed droplets in an emulsion are in constant motion and there are frequent collisions between them in absence of steric and/or electrical barrier. These collisions lead to droplets aggregation and, if the interfacial wall is broken, to an irreversible coalescence of the droplets. In C/W emulsion, this kind of barrier can be easily created, as this is done in O/W emulsion. Unfortunately, in W/C emulsion, it is very difficult to obtain such barrier without the use of surfactants containing fluoroalkyl or fluoroether tails [16]. As a matter of fact, few polymers are soluble enough in CO_2, except fluoropolymers, siloxane and

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* Corresponding author. Tel.: +33 2 41 73 58 48; fax: +33 2 41 73 58 03.
E-mail address: frank.boury@univ-angers.fr (F. Boury).

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polycarbonate to create a steric barrier. Furthermore, CO_2 has a low dielectric constant, which renders difficult the creation of an electrostatic barrier.

Consequently, in a CO_2 medium, without the use of very CO_2-phile surfactants often containing a fluorinated-tail, aqueous droplets frequently interact and coalesce when the interfacial wall is broken. 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 tends 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 (E_e), which describes surfactant interactions in the interfacial layer (i.e. lateral interaction). A non-equilibrium elasticity (E_{ne}) that can be related to the interactions of surfactant with adjacent phases (i.e. desorption and reorganization of the interface), associated with a relaxation time τ representing the necessary time for the interface to reach a new equilibrium energetic state after the perturbation.

We have previously investigated the formation of pure water–CO_2 interface by means of a drop tensiometer [1,17]. We have described it as a two-step phenomenon. Firstly, the CO_2 molecules quickly adsorb onto the water surface for equilibrating their chemical potential between the bulk CO_2 and the water surface. This physisorption leads to the interaction of one CO_2 molecule with one H_2O molecules. Secondly, CO_2 molecules diffuse into the water subsurface and then modify the water organization. This reorganization of the water molecules creates a network of H_2O–CO_2 clusters to form an interphase and leads to a decrease of γ until an equilibrium state. These H_2O–CO_2 clusters are formed at temperature upper (20–40 °C) to the one usually described as the limit (10 °C) for the formation of the crystalline structure called clathrate hydrate [18–20].

Elasticity measurements and macroscopic visualization suggest that the growing of clusters is driven by assembly of many small blocks and accelerates with the CO_2 pressure. Their interfacial concentration and their size increase with time until the saturation of the interface.

A fundamental understanding of interfacial surfactant adsorption and the rheological properties of H_2O–CO_2 interface is then useful for designing surfactants that stabilize efficiently W/C emulsions.

This must be performed by first understanding the rheological comportment of the pure H_2O–CO_2 interface and then by the measurement of interfacial properties in presence of different surfactants.

We described in this paper the measurement of rheological parameters of H_2O–CO_2 interface in presence of small or macromolecular adsorbed molecules. We compared two kinds of rheological approach consisting either of a sinusoidal or a ramp interfacial area perturbation.

2. Materials and methods

2.1. 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 consists in a view cell under CO_2 atmosphere, a light source, a CCD camera, a computer, a syringe (Exmire microsyringe MS*GLL100, ITO corporation, Japan) and a motor as described by Tewes and Boury [1,2,17]. The syringe was filled with pure water and coupled to the view cell. Then, the view cell was pressurized with pure CO_2 until reaching the desired temperature (40 °C) and pressure. After that, the system is left during 24 h for equilibrating the water phase with the CO_2 phase. Pendant drops whose area is controlled during all the time of experience by the motor were formed at the end of a stainless steel needles (needles 20 G, popper, USA), having an inside diameter of 1 mm and connected to the syringe.

2.2. Rheological measurements

A rheological experiment is performed by applying a controlled perturbation to the interface in order to simultaneously follow the related interfacial pressure variations, $\Delta\pi = \gamma(t) - \gamma_i$, with γ_i is the interfacial tension before the perturbation and $\gamma(t)$ the interfacial tension during or after the perturbation. In this study, the viscoelastic response of an interfacial film to a dilatational mechanical strain (ramp or sinusoidal) in the time scale of 1–10^3 s is studied by means of two experimental approaches.

2.2.1. Ramp type perturbation approach

The first approach consists to realize two types of continuous and monotonic compression of the equilibrated interfacial layer

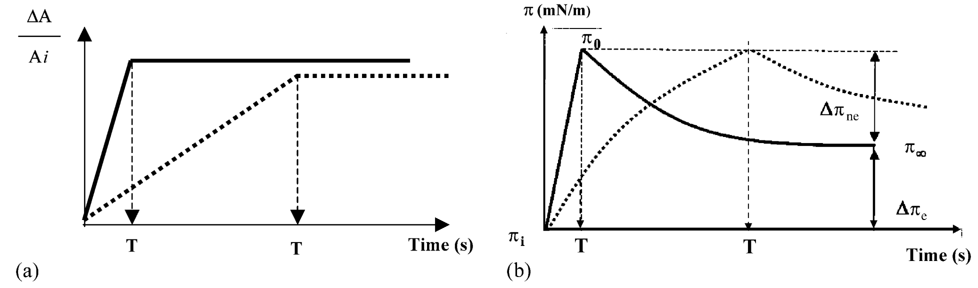

Fig. 1. Relative area (a) and interfacial pressure change $\Delta\pi$ (b) occurring during the time T of compression (bold line: fast compression; dashed line: slow compression).