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Dynamic properties of Span-80 adsorbed layers at paraffin-oil/water interface: Capillary pressure experiments under low gravity conditions

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ABSTRACT

Measurements by capillary pressure tensiometry, under microgravity conditions aboard the International Space Station, supplied a consistent set of reliable results for the dynamic interfacial tension and for the interfacial dilational viscoelastic modulus, quantitatively characterizing the dynamics of Span-80 adsorbed layers at the paraffin-oil/water interface.

The experiments were executed at three different temperatures, i.e., 20, 30 and 40 °C, according to a pre-established built-in time-line in the orbiting facility. The interfacial area was subjected to perturbations with various functional forms (square pulses, ramps and harmonic oscillations), at three consecutive amplitudes (5%, 10% and 20%). Each experiment was performed in three successive repetitions, in view of an advantageous telemetered data redundancy.

The interfacial responses to imposed perturbations, for the studied minimal surfactant concentration of Span-80 in paraffin-oil (that is $(2 \div 3) \times 10^{-5}$ mol/dm^3) revealed a diffusion-controlled adsorption mechanism, definitely matching the Lucassen & Van den Tempel model in the frequency-domain representation. The interfacial responses also showed a linearity range up to the 20% amplitude.

Interfacial relaxation responses to transient interfacial perturbations substantially validated the diffusion-controlled model for the adsorption mechanism, in the time-domain representation.

1. Introduction

The dynamic behavior of adsorbed layers at fluid interfaces is manifested and quantitatively expressed by the measured values of dynamic interfacial tension, γ(t), and of interfacial dilational viscoelastic modulus, ε*(iω), as a function of time t and of angular frequency ω, respectively [1–3].

These two physical quantities, γ(t) and ε*(iω), are important parameters in a large variety of industrial processes involving multiphase systems, characterized by high specific interfacial area, like foams and emulsions [3]. Dealing in particular with water/hydrocarbon systems, since the second half of the 20th century up to nowadays, γ(t) and ε*(iω) are recognized as relevant properties in crude oil technology (e.g., in enhanced oil recovery, oil transport, oil/water emulsion formation and breaking, emulsion-stability control, oil de-watering, emulsion/sludge separation in waste water treatment, etc., [4–18]).

Several studies are reported in the literature aiming at a deeper understanding of the fundamental laws governing the above-specified dynamic behavior of adsorption layers occurring in real systems (ref. [19], and references therein).

However, a multitude of particular circumstances is still insufficiently investigated and there is a number of open discussions about the interpretation models.

Now it is ascertained that distinct mechanisms concur to determine the time-evolution of surfactant adsorption layers [19]. Certainly, physical or empirical models are adequately representative of the real systems in case these models are derived on a large experimental basis, that is, on phenomenological observations and consistent measurement values, as obtained by different well-assessed experimental methodologies.

Actually, along with traditional laboratory studies on oil/water adsorption layers, experiments aboard orbiting vehicles definitely result in reliable significant information on the interfacial properties, in particular on the dynamics of adsorbed layers at the oil/water interface,

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by virtue of a unique environment where concomitant gravity effects are absent.

Indeed on-ground gravity-driven convection, caused by temperature or concentration gradients, may deform the bulk diffusion profile near the interface, confusing the data interpretation. Instead, in space, the microgravity environment grants convection absence and hence no distortion of the diffusion path, that is, microgravity is beneficial as it provides diffusive conditions that are ideal for testing models and measuring specific parameters related to surfactant transport. In this connection, as an additional advantage, the effects driven by capillary forces and the differences in chemical potentials are enhanced [20].

Microgravity also provides drop interfaces of constant-curvature. Then a) the adsorption process takes place at a perfectly spherical interface and b) the normal modes of oscillation are exclusively radial (i.e., prolate/oblate oscillation modes are not triggered).

During the recent years, the European Space Agency (ESA) promoted the project “FASES” (acronym for “Fundamental and Applied Studies of Emulsion Stability”) with the objective of establishing a link between emulsion stability and the physico–chemical characteristics of droplet interfaces, of emulsion films, and the modeling of emulsion dynamics.

Hence, drop-interface experiments were conducted under the favorable microgravity conditions in space, using a Capillary Pressure Tensiometer (denoted as FAST, i.e., Facility for Adsorption and Surface Tension), aboard the National Aeronautics and Space Administration (NASA) Discovery shuttle in 1998 [21] and the Columbia shuttle in 2003 [22].

More recently, investigations within the “FASES” Project demonstrated the specific influence of nanoparticles and of different surfactants (including Span-80, i.e., sorbitan monooleate,) in tuning the inner structure of water/paraffin-oil emulsions, on account of the pertinent interfacial properties [23–25]. In the framework of these investigations, experiments on diluted and on concentrated water/paraffin-oil emulsions with Span-80 were conducted aboard the International Space Station (ISS) in the Fluid Science Laboratory of the Columbus Modulus, from June 2013 to June 2014.

Moreover, from April to August 2014, an improved flight facility (denoted as FASTER) accomplished scientific experiments on liquid/liquid interfacial layers operating on board of the ISS (European Drawer Rack of Columbus Modulus). The examined systems were water/hydrocarbon interfaces (i,e., water/paraffin-oil and *n*-hexane/water) with different concentrations of standard non-ionic surfactants and at different temperatures.

Extracting a fraction of the obtained data from the above-mentioned microgravity experiments, in this article we focus the interest on the interfacial dynamic properties of the single interface, created between a drop of pure water and a matrix-solution of Span-80 in paraffin-oil, at low surfactant concentrations (i.e., $c = 0.02 \div 0.03\ \mu\text{mol/dm}^3$) at different temperatures and at different time-dependent coverage of the adsorbed layer. The specific aim is to provide a contribution for characterizing the viscoelastic behavior of water/oil interfaces and for revealing the mechanism of bulk-interface mass transport in water/hydrocarbon systems containing simple surfactants.

Achievement of such a target is significant for advancing fundamental knowledge, that may also issue in a fruitful transmutation of know-how into industrial operations, involving two-phase liquid systems with minimal surfactant concentration.

2. Experimental technique and procedure

2.1. Capillary pressure tensiometry

Capillary pressure tensiometry (CPT) is a reliable technique for the measurement of the interfacial dynamic properties γ(t) and ε*(iω) [26–29]. Such a technique is particularly effective when operating aboard orbiting vehicles, that is, in absence of hydrostatic pressure and of density-driven convection [22,30,31]. CPT is based on the fundamental law of the Laplace equation, allowing the determination of γ(t) by measuring the capillary pressure of a droplet (i.e., the differential Δp (t) pressure across the droplet interface) and the concomitant droplet radius r(t)

$$\gamma(t) = \frac{\Delta p(t) \times r(t)}{2} \tag{1}$$

provided the assumption that in space any imposed change of r(t) maintains in the droplet a spherical cap-shape geometry, specifically the assumption that just pure radial normal oscillation modes are generated in case of imposed sinusoidal oscillations of the radius.

In synchronism with the imposed radius, the interfacial area of a sinusoidally oscillating droplet is also easily measured, by virtue of the spherical geometry. Hence the complex interfacial dilational viscoelastic modulus is determined, according to the following definition expression in the frequency domain [32]

$$\varepsilon^*(i\omega) = \frac{\Delta\gamma \times \exp[-i(\omega t + \phi)]}{\Delta A \times \exp(-i\omega t)/A_0} = |\varepsilon^*| \times (\cos(\phi) + i \times \sin(\phi)) \tag{2}$$

where ω represents the angular frequency, Δγ × exp[-i(ωt + ϕ)] the interface response to the imposed area perturbation ΔA × exp(-iωt)/A0, Δγ and ΔA the oscillation amplitudes of the interfacial tension and the interfacial area, respectively, ϕ the phase shift between perturbation and response, A_0 the mean interfacial area of the sinusoidal cycle and |ε*| is the modulus of the complex number ε*(iω).

In time-intervals of moderately changing droplet dimension, as well as in low frequency ranges, γ(t) and ε*(iω) are obtained by the simple expressions of Eqs. (1), (2). At increasing changing rates, or oscillation frequencies, additional hydrodynamic pressure components (i.e., Poiseuille and inertial pressure) gradually overlay the capillary pressure, hence appropriate extended calculations were recently developed (see details in refs. [22,27,33]).

Fig. 1 illustrates the structure and the essential parts of the FASTER facility, that is, the devised and engineered capillary pressure tensiometer for space experiments. The measurement cell consists of two chambers (pure water reservoir and matrix-cell) connected through a capillary. The volume of the reservoir is about $v = 5.6\ \text{cm}^3$ and of the matrix-cell is about $V = 68.5\ \text{cm}^3$.

The water/hydrocarbon interface is generated by withdrawing from the pure-water reservoir a droplet inside the hydrocarbon matrix by means of a piezo-actuator. The piezo-actuator also controls the drop dimensions (i.e., radius and interfacial area extension) according to pre-established time-functions. A CCD-camera and different sensors in synchronism acquire the values of the relevant physical quantities, namely, temperature, differential Laplace-pressure, and geometrical properties of the drop. Two syringes allow injection of surfactant into the matrix liquid.

Hydrodynamic instability of the droplet [30,34] is prevented due to under-vacuum liquid-filling of all cell-compartments, averting the unfavorable presence of air microbubbles.

2.2. Materials

Pure water (purity level MilliQ) was produced by a Millipore (Elix plus MilliQ) purification chain, provided with ultraviolet ray irradiation.

Paraffin-oil was purchased from Fluka, cat.n. 76235 (CAS DataBase reference 8012-95-1, density $d = 0.86\ \text{g/cm}^3$, dynamic viscosity 100–145 mPa s at 20 °C) and used without further purification.

Span-80 (Sorbitan monooleate) was purchased from Merck, cat.n. 840123 (CAS DataBase reference 1338-43-8, density $d = 0.994\ \text{g/cm}^3$ at 20 °C).

The concentration of Span-80 in the syringe is $c = 0.0348\ \text{mol/dm}^3$.