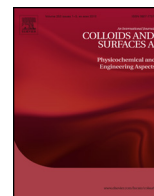




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# Emulsions stabilized by the interaction of silica nanoparticles and palmitic acid at the water–hexane interface

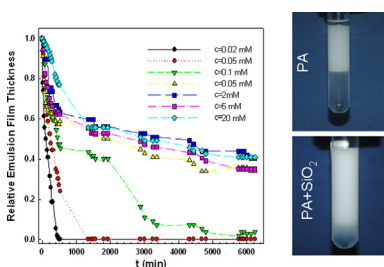
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### HIGHLIGHTS

- Palmitic acid and silica nanoparticles at the water–hexane interface.
- Emulsions between silica nanoparticle dispersions and palmitic acid hexane solutions.
- Emulsion stabilization by the formation of nanoparticle–surfactant complexes at the droplet interface.
- Dependence of emulsion stability on the liquid phases volume ratio and palmitic acid content.
- Nanoparticle–surfactant complexes redispersion for surfactant adsorption on the nanoparticle exceeding the monolayer.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The interaction between palmitic acid (PA) and silica nanoparticles at the water/hexane interface has been studied in relation to the ability in the stabilization of water in oil emulsions. To this aim, emulsions formed by aqueous silica nanoparticle dispersions and PA solutions in hexane have been investigated. In contrast with other previous studies, where the interaction of nanoparticles and surfactant molecules occurs already in the bulk phases, here PA and silica nanoparticles are dissolved/dispersed in different phases and interact only at the liquid–liquid interface. As for other particle-stabilized emulsions, the investigated system can provide emulsions stable over very long time because of the formation of nanoparticle–surfactant complexes, which accumulate at the droplets interface, providing a steric hindrance of coalescence. However, the present study has pointed out that these enhanced stability conditions are achieved only when the amount of surfactant leads to the formation of single surfactant layers onto the particles surface. Whereas an excess surfactant amount interacts with the particles, the formation of multilayers would be possible, and the formed complexes can be redispersed again in the aqueous bulk phase. This recalls to a scenario where the degree of hydrophobization of the particles is critical for the emulsion stabilization. This can be easily tuned by the control of the surfactant concentration and the volume ratio between the liquid phases. Interfacial tension measurement of the same couple of liquids, has allowed us to explore in more detail such phenomena, revealing a non-monotonic evolution of the dynamic interfacial tension at large PA concentrations. Also these observations can be rationalized assuming the redispersion of the complexes mentioned above, which allows explaining the interfacial tension evolution on the basis of the succession of adsorption and desorption of the different species – nanoparticles, nanoparticle–PA complexes, PA molecules – involved.

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## 1. Introduction

Particles at fluid interfaces is a research topic with important implications in numerous technological applications that deal with the stabilization of foams, emulsions, bubbles or liquid membranes [1–5]. Besides, the request of new porous material production needs a better understanding of how the solid particles adsorb at the fluid interface modifying the interfacial properties, and affecting the final structure of the product [6–8].

In fact, particles are able to irreversibly adsorb at fluid interfaces dampening the coalescence of drops/bubbles not only by a steric effect but also influencing the interfacial properties of the considered system. In particular, the presence of solid particles may affect the surface tension and dilational and shear viscoelastic behaviour of the fluid interface [9–15].

It is well-established that the segregation of micro and nanoparticles to a fluid–fluid interface can be used to stabilize the so-called Ramsdem–Pickering emulsions due to the formation of a solid-like armour that prevents the drop coalescence [16–20]. The presented study is focused on the formation and stability of water/hexane emulsions of palmitic acid (PA) in the presence and absence of silica nanoparticles. Limage et al. [21,22] and Worthen et al. [23] pointed out the ability of similar nanoparticles to stabilize emulsions by their interaction with other surfactants. The here studied system has been chosen due to interesting behaviours observed in previous works [24–26], where different types of interfacial layers composed by PA and silica particles have been investigated, namely: PA spread at the silica dispersion–air interface, PA plus silica aqueous phase against air surface, PA in hexane versus aqueous silica dispersion interface. The results point out the formation of complexes between the hydrophobic surfactant and the hydrophilic particles at the fluid interfaces.

In a recent work, Whitby et al. [27] have analyzed the importance of the synergetic interaction between an oil-soluble surfactant (octadecylamine) and silica nanoparticles on the stabilization of the interface. The case of PA dissolved in hexane in contact with an aqueous dispersion of silica is particularly relevant because allows studying the transfer of the two species through the interface and their resulting organization once adsorbed. The deepening of these scientific aspects is the objective of the present paper, in which the interfacial properties of oil PA solutions against water or silica aqueous dispersion are correlated with the formation and stabilization of the corresponding water in hexane emulsions.

## 2. Materials

Palmitic acid (PA) was purchased from Sigma–Aldrich (Germany) with a purity higher than 99% and used without further purification. Hexane of spectro-photometric grade purity (Merck, Germany) was used to prepare the PA solutions. Water used was produced by Millipore (Elix+Milli-Q) purification system. The purity degree of the solvents was tested by surface/interfacial tension measurements. Stable values of 72.5 mN/m and 51.0 mN/m were found for air/water and water/hexane interfaces, respectively.

Hydrophilic silica nanoparticle dispersions containing 1 wt% of solid content were obtained by dilution of a commercial dispersion of Levasil 200/30 (30.38 wt% of solid content) produced by H.C. Starck/Bayern (Germany). These negatively charged particles ( $\xi$ -potential =  $-42 \pm 5$  mV) present a quite monodisperse size distribution with an average diameter of  $15 \pm 2$  nm and a specific surface area of 200 m<sup>2</sup>/g. The dispersions do not contain surface active agents and are stable against flocculation and sedimentation by the sole effect of the large particle hydrophilicity, which

also rules out their segregation at the aqueous interface. In fact, any change on the surface/interfacial tension in respect to pure water can be detected for the silica dispersion/air and silica dispersion/hexane interfaces.

## 3. Methods

### 3.1. Interfacial tension measurements

Measurements of dynamic and equilibrium interfacial tension ( $\gamma$ ) were performed by a Profile Analysis Tensiometer (PAT1-Sinterface, Germany) at water/hexane interface. The method is based on the acquisition of the profile of a drop formed at the tip of a steel capillary, immersed in a glass cell containing the second liquid phase. The  $\gamma$  value is obtained by the fitting of the acquired profile of the axis-symmetric drop with the Bashforth–Adams equation. More details on this technique can be found in Ref. [28].

The measurements were carried out with pendant drops of pure water or of the 1% aqueous silica nanoparticle dispersion in the hexane PA solutions. All measurements were performed at 20 °C.

### 3.2. Emulsion preparation

Emulsions with a total volume of 10 mL were prepared with different hexane phase volume fraction,  $x = V_h/(V_h + V_a)$ , ranging between 0.1 and 0.9, where  $V_h$  is the volume of hexane phase and  $V_a$  is the one of the aqueous phase. The amount of PA in the hexane solution was in the range of concentration ( $c$ ) between 0.02 and 20 mM, being the aqueous phase either pure water or the 1% silica nanoparticle dispersion described above. Emulsions were prepared by the laboratory mixer (IKA ULTRA TERPAX T25) at 10,000 rpm for 10 min, in a test tube with the diameter of 15 mm. The adopted emulsification procedure does not provide complete emulsification of the samples, but create different amounts of emulsion, depending on  $c$  and on  $x$ . The results reported here focus on the stability of the emulsified fraction, quantified on the basis of the time evolution of the height of the emulsion column.

The emulsion samples checked by an optical microscope show always rather concentrate and monodisperse droplets, with a diameter of the order of 20  $\mu$ m. Diluting these samples with hexane on the microscope slide provides separate droplets, after the evaporation of the matrix. Emulsions are therefore always of water-in-oil type.

## 4. Results and discussion

### 4.1. Emulsion stability

We analyze hereafter the effect on the emulsion stability of the PA concentration and of the ratio between the hexane phase and the water phase in the initial mixture.

As expected, emulsification was observed only in the presence of PA. In fact, it is well known that the bare silica nanoparticles are unable to stabilize any water–oil emulsion due to their high hydrophilicity that prevents their segregation to the drop interface [29,30].

#### 4.1.1. Effect of silica nanoparticles and PA concentration on the emulsion stability

The effect of PA concentration was investigated on emulsion with  $x=0.5$ . Fig. 1a and b shows the variation of the thickness of the emulsion column with time in the absence and presence of nanoparticles, respectively, for two different PA concentrations.

The presence of PA in the hexane phase allows water-in-hexane emulsions to be stabilized. However, the stability of these

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