



## Effect of [CTAB]–[SiO<sub>2</sub>] ratio on the formation and stability of hexadecane/water emulsions in the presence of NaCl

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### ABSTRACT

The formation and stability of hexadecane (H)/water (W) emulsions stabilized by mixtures of cetyltrimethylammonium bromide (CTAB) and SiO<sub>2</sub> particles in decreasing ratios (R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>) in presence of NaCl at constant ionic strength as a co-stabilizer was investigated. Interfacial creep compliance-time studies of the CTAB–SiO<sub>2</sub> films at the H–W interface were carried out in order to understand the mechanisms of the CTAB–SiO<sub>2</sub> aggregates adsorption and their interactions at the H–W interface. The characterization and stability of H-in-W emulsions (E-R<sub>1</sub>, E-R<sub>2</sub>, E-R<sub>3</sub>) was determined by the combination of light scattering diffraction, DSC and optical microscopy techniques. The emulsions displayed polydisperse droplet size and the average droplet size of the emulsions decreased as the CTAB–SiO<sub>2</sub> ratio diminished. DSC aging tests indicated that only emulsions made with R<sub>3</sub> presented changes in the average droplet size probably due to slower reorganization of the clusters at the droplet interface until a well structured film was developed. Despite that E-R<sub>1</sub> and E-R<sub>2</sub> presented a relatively large non-spherical droplets they were highly stable against coalescence due to the formation of a solid-like interfacial layer.

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### 1. Introduction

Pickering emulsions are surfactant free dispersed systems stabilized by the adsorption of solid particles at the oil–water interface with a wide variety of potential applications including biomedical materials, pharmaceuticals, electronics, photonics, cosmetics, functional food and coatings [1–3]. In contrast to conventional emulsions, which are usually thermodynamically unstable and stabilized by surfactants or amphiphilic linear copolymers, Pickering emulsions are often super-stable due to the nearly irreversible adsorption of the colloidal particles at the oil/water interface because of their high energy of attachment, which makes the final emulsions extremely stable with shelf life stabilities of months or even years [2,4,5].

In Pickering emulsions, the particles are wetted partially by oil and partially by water so they become surface-active molecules, where the driving force for formation of emulsion droplets is the preference of particles to reside at oil–water interfaces. Partially hydrophobic solid materials, such as silica, stabilize oil-in-water (O/W) emulsions with non-polar oils ( $\theta_{O/W} < 90^\circ$ ) and water-in-oil (W/O) emulsions with more polar oils like esters or alcohols

( $\theta_{W/O} > 90^\circ$ ) [5]. The main stabilization mechanisms of solid particles in emulsions are related with the formation of (a) an adsorbed dense film (monolayer or multilayer) around the dispersed droplets impeding coalescence by providing a strong repulsion energy term due to steric hindrance, and (b) 3D particle network due to formation in the continuous phase due to particle–particle interactions in which the oil droplets are captured and more or less immobilized [5,6].

However, the use of solid particles presents drawbacks in relation to surfactants in emulsion stabilization. Due to the small size of surfactant molecules, they tend to adsorb at the interface at a faster rate than solid particles and this mobility represents a real advantage in terms of emulsion formation, so while the surface area of the dispersed phase is increased, the emulsifiers adsorb and stabilize the developed “naked” interface area before incipient coalescence occurs, being more efficient than solid particles [7,8]. In addition, surfactants are capable to decrease the water–oil interfacial tension whereas solid particles do not. It can be seen that the properties of surfactants and solid particles as emulsifiers are completely different and consequently emulsions stabilized by particles present different rheological and interfacial properties from classical emulsions stabilized by surfactants.

An ongoing research topic is to combine the use of surfactants and solid particles in the formation and stabilization of emulsions in a drive to provide new functional properties that

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**Table 1**

Composition, zeta potential and pH of the dispersions.

Dispersion code	SiO <sub>2</sub> (g L <sup>-1</sup> )	CTAB (g L <sup>-1</sup> )	NaCl (g L <sup>-1</sup> )	CTAB:SiO <sub>2</sub> ratio	Zeta potential (mV)	pH
R <sub>1</sub>	16.55	1.63	10.0	0.098	-8.75 ± 1.21	9.80
R <sub>2</sub>	21.80	0.99	10.0	0.045	-23.10 ± 1.14	10.47
R <sub>3</sub>	27.05	0.36	10.0	0.013	-27.90 ± 1.25	10.57
SiO <sub>2</sub>	300.00	-	-	-	-31.20 ± 1.30	11.00

cannot be achieved by using either emulsifying agents on their own. Surfactants can modify the wettability of solid particles by adsorbing onto their surface, changing their hydrophobicity and promoting a stronger particle–particle interaction and adsorption at the oil–water interface, giving as a result more stable emulsions [9–12]. Moreover, the presence of additives in emulsion systems like electrolytes, which modify the particles charge and flocculation properties, may promote the adsorption of surfactant molecules at both solid–liquid and liquid–liquid interfaces [13]. Although substantial progress has been made in understanding the role that several factors play on the stability of Pickering emulsions, there are few works dealing about the influence of solid particles, surfactants and electrolytes, and the relative ratios between them, on the stability of Pickering emulsions.

Recently, differential scanning calorimetry (DSC) has emerged as an alternative to microscopy or light scattering techniques for characterizing emulsions (non-diluted emulsions in particular), without disturbing the system, and providing qualitative information on droplet size, their polydispersity and size evolution over time within a single experiment [14,15]. The application of shear deformations to interfacial layers give indirect information of inter- and intramolecular interactions taking place between surfactants, biopolymers, solids, and in general compounds adsorbed and spread-out at the interfacial layer. The understanding of these interactions permit to have control over the structure and, hence understand the role they play in defining the properties of the system [16].

The objectives of this work were to investigate the effect of the interactions between silica nanoparticles and cetyltrimethylammonium bromide on the shear viscoelastic properties of interfacial films as well as the effect of [CTAB]–[SiO<sub>2</sub>] ratios upon the formation and stability of hexadecane in water emulsions in the presence of NaCl at constant ionic strength.

## 2. Materials and methods

Hexadecane reagent grade and cetyltrimethylammonium bromide (CTAB) were purchased from Sigma–Aldrich Quimica (Toluca, State of Mexico, Mexico). The colloidal dispersion of silica nanoparticles (SiO<sub>2</sub>; 30% (w/w); Bendzil 830CC; pH ~ 11; Akzonobel) was provided by Silicatos y Derivados, S.A. de C.V. (Tlalnepantla, State of Mexico, Mexico). Sodium chloride (NaCl) was purchased from J. T. Baker, S.A. de C.V. (Xalostoc, State of Mexico, Mexico). Deionized water (W) was used in all the experiments.

### 2.1. Characterization of CTAB–SiO<sub>2</sub> aggregates

#### 2.1.1. Size distribution

Three aqueous SiO<sub>2</sub>–CTAB–NaCl dispersions were prepared by putting the requisite amounts of the three components in water with magnetic stirring for 5 h [17], obtaining the dispersions R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> whose composition is given in Table 1. The concentrations and ratios for SiO<sub>2</sub>, CTAB, and NaCl used in this work were more or less in the range on those reported by Schmitt-Rozières et al. [17], who reported that the [CTAB]–[SiO<sub>2</sub>] ratio is an important parameter that controls the shape, geometry and changes from spherical to polymorphous of the droplets. The volume frequency of particle

size distribution of the aggregates formed in R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> were measured with a Malvern Mastersizer 2000 (Malvern Instruments Ltd., Malvern, Worcestershire, UK), using water (refractive index 1.33) as dispersant. Measurements were done in fresh dispersions and after submitting them to 2 min of sonication with a Sonics Vibra Cell VCX 130 PB sonicator (Sonics & Materials, Inc., Newtown, CT, USA) at 55% amplitude, in order to observe changes in particle size due to aggregation/disaggregation phenomena.

#### 2.1.2. Zeta potential

The zeta potential of the SiO<sub>2</sub> colloidal dispersion and of R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> (diluted to half-ionic solution strength for obtaining reliable readings) was measured in the Nano Zetasizer (Malvern Instruments Ltd., Malvern, Worcestershire, UK). The pH of all the dispersions was measured with a pH-meter (Conductronic Mod. 10, Conductronic, S.A., Puebla, State of Puebla, Mexico).

#### 2.1.3. Interfacial films rheology

The interfacial rheological measurements were done in accordance to the procedure described by Román-Guerrero et al. [18] with slight modifications. A Physica MCR 300 (Physica Mebtechnik GmbH, Stuttgart, Germany) modular compact rheometer coupled to a stainless steel biconical disk (radius of disk, R<sub>b</sub>, of 15 mm and disk double angle, 2α, of 10°) was used for this purpose. A thermostated acrylic vessel (inner radius, R<sub>c</sub>, of 27 mm) was inserted in the measuring plate of the rheometer. R<sub>1</sub>, R<sub>2</sub> or R<sub>3</sub> (30 mL) were carefully spilled into the vessel. Afterwards, the rheometer motor drive was lowered until the stainless steel biconical disk was placed at the aqueous dispersion surface. Then 30 mL of H were carefully poured with help of a glass rod onto the vertical wall of the vessel until the oil phase formed a layer above the aqueous dispersion. The resulting interfacial films were coded F-R<sub>1</sub>, F-R<sub>2</sub>, and F-R<sub>3</sub>, respectively.

##### 2.1.3.1. Interfacial static viscoelastic properties (creep compliance).

The interfacial creep compliance was carried out by subjecting the film to a constant interfacial shear stress ( $\sigma^{\text{int}}$ ) of 0.3535 mN/m during 15 min, after which  $\sigma^{\text{int}}$  was withdrawn, and the stress relaxation of the film was followed for further 15 min. The change in the steady rotational speed and angular displacement of the disk with time ( $\theta_b$ ) was monitored every 2 s with the rheometer software and the interfacial shear strain ( $\gamma^{\text{int}}$ ) as function of time was calculated with Eq. (1). The interfacial compliance of the films as function of time ( $J(t)$ ) was obtained with the following Eq. (2):

$$\gamma^{\text{int}} = \frac{2R_b^2}{R_c^2 - R_b^2} \theta_b \quad (1)$$

$$J(t) = \frac{\gamma^{\text{int}}(t)}{\sigma^{\text{int}}} \quad (2)$$

where  $\sigma^{\text{int}}$  was evaluated at the disk radius (R<sub>b</sub>), and R<sub>c</sub> is the vessel radius. Plots of  $J(t)$  versus  $t$  for R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> interfacial films were obtained. The experimental data were non-linearly adjusted to the following equation (3) [19] using a Polymath software release 6.1 (Cache Corporation, Austin, TX, USA):

$$J(t) = J_0 + J_m(1 - e^{-(t/\lambda_m)}) + J_N \quad (3)$$

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