

Study of Synergistic Interactions Between SiO₂ Nanoparticles and CTAB in the Presence of NaCl: Relationships with the Formation and Stabilization of Hexadecane-in-Water Emulsions

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ABSTRACT

Hexadecane/water emulsions were prepared with different mixtures in decreasing ratios (R1, R2 and R3) of silica particles (SiO₂) and cetyltrimethylammonium bromide (CTAB) to determine droplet crystallization transitions upon freezing by differential scanning calorimetry (DSC), droplet size distribution, and the rheological properties, in order to study the effect of the [CTAB]/[SiO₂] ratio in the formation process and stability of the emulsions. The emulsions were polydisperse and the average droplet size of the emulsions decreased as the [CTAB]/[SiO₂] ratio diminished. DSC ageing tests indicated that only the emulsion prepared with R3 (E-R3) presented changes in the average droplet size probably due to a reorganization of the CTAB-SiO₂ aggregates at the droplet interface until a well-structured film was developed. Despite that E-R1 and E-R2 presented relatively large non-spherical droplets they were highly stable against coalescence due to the formation of a solid-like interfacial layer.

Keywords: silica nanoparticles, cetyltrimethylammonium bromide, interfacial rheology, hexadecane-in-water emulsions, calorimetry

1 INTRODUCTION

Recently there has been an emerging interest for the production of a wide range of hybrid colloid materials using various types of nanoparticles as solid stabilizers of emulsions [1]. Compared to surfactants, their properties are completely different in terms of diffusion, adsorption at the water-oil interface as well as their interfacial behavior [2]. However, the combination in the use of surfactants and solid particles in the formation and stabilization of emulsions can provide new functional properties that cannot be achieved by using either emulsifying agents on their own. Surfactant can modify the wettability of solid particles due to their adsorption onto the surface, changing the particle hydrophobicity promoting a stronger particle-particle interaction and adsorption at the water-oil interface leading to the formation of more stable emulsions.

Although substantial progress has been made in understanding the mechanisms of emulsion stability by particles and their interactions with surfactants, there is still open questions about the role of several factors in

stabilizing Pickering emulsions in particular with the influence of solid particles, surfactant and electrolytes and the ratio between them on emulsion stability.

This work deals with the study of the synergistic interactions between silica (SiO₂) particles and a surfactant cetyltrimethylammonium bromide (CTAB) on the shear viscoelastic properties of the hexadecane-water (H/W) interfacial films and the formation and stability of emulsions.

2 MATERIALS AND METHODS

A colloidal solution of silica nanoparticles with a pH value of 11 (30 wt%, Bendzil 830CC, Akzonobel) provided by Silicatos y Derivados S.A. de C.V., Mexico City, Mexico, was used to prepare the H/W emulsions. Hexadecane reagent grade and cetyl triethylammonium bromide (CTAB) surfactant were purchased from Sigma-Aldrich Quimica (Toluca, State of Mexico, Mexico). Sodium chloride (NaCl) was purchased from J.T. Baker, S.A. de C.V. (Xalostoc, State of Mexico, Mexico).

2.1 Characterization of the CTAB-SiO₂ aggregates

The aqueous outer phases of the emulsions R1, R2 and R3 were prepared as followed: 10 g of NaCl were put into a volumetric flask and dissolved with enough water, then the requisite amounts of CTAB and SiO₂ colloidal solution were added and the solutions were diluted with water to complete 1 L in order to obtain the [CTAB]/[SiO₂] ratios indicated in table 1. Finally, these solutions were stirred under magnetic stirring during 5 h.

The volume frequency of particle size distributions of the aggregates were measured with a Malvern Mastersizer 2000 (Malvern Instruments Ltd. Malvern, Worcestershire, UK) using water as dispersant.

	NaCl (g.L ⁻¹)	[CTAB]/[SiO ₂] ratio	Zeta Potencial (mV)	pH
R1	10.0	0.098	- 8.75 ±1.21	9.80
R2	10.0	0.045	- 23.10± 1.14	10.47
R3	10.0	0.013	-27.90 ±1.25	10.57
SiO ₂	-	-	-31.20± 1.30	11.00

Table 1: Composition, zeta potential and pH of the outer phases of H/W emulsions.

The measurements were done in fresh dispersions after submitting them to sonication with a Sonics Vibra Cell

VCX 130 PB sonicator (Sonics & Materials, Inc., Newtown, CT, USA) at 55% amplitude and frequency of 20 kHz during 2 min.

The zeta potential of the colloidal dispersions R1, R2 and R3 was measured in the Nano Zetasizer (Malvern Instruments Ltd., Malvern, Worcestershire, UK). The pH was measured with a pH-meter (Conductronic Mod. 10, Conductronic, S. A., Puebla, Mexico).

2.2 Interfacial Films rheology

A physica MCR 300 modular compact rheometer (Physica Mebtechnik GmbH, Stuttgart, Germany) coupled to a stainless steel biconal disk of radius $R_b = 15\text{mm}$ and with a double angle 2α of 10° was used to interfacial properties of the water-oil interfaces formed by the aggregates. A thermostated acrylic vessel with an internal radius $R_c = 27\text{ mm}$ was inserted in the measuring plate of the rheometer. 30 ml of colloidal solutions was carefully poured into the vessel. Then the biconical disk was placed at the aqueous surface using the rheometer drive motor. Finally, 30 ml of hexadecane was poured carefully using a glass rod above the aqueous solution. The interfacial creep compliance was carried out by subjecting the film to a constant interfacial shear stress (σ_{int}) of 0.3535 mN/m during 15 min, after which σ_{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 (θ_b) was monitored every 2 s with the rheometer software and the interfacial shear strain (γ_{int}) as function of time was calculated with Eq. (1).

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

The interfacial compliance of the films as function of time ($J(t)$) was obtained with the following Eq. (2)

$$J(t) = \frac{\gamma_{\text{int}}(t)}{\sigma_{\text{int}}} \quad (2)$$

where σ_{int} was evaluated at the disk radius R_b and R_c is the Wessel radius. Plots of $J(t)$ versus t for R1, R2, and R3 interfacial films were obtained.

2.3 Preparation of the emulsions

The H/E emulsions were prepared in two-stage emulsification procedure. In the first step, 0.2 dispersed phase mass fraction H/W emulsions were prepared, using the different aqueous outer phase (R1, R2 and R3). The hexadecane was dripped into the aqueous phase and homogenized with an Ultra-Turrax T10 basic (IKA®-WERKE Works Inc., Wilmington, NC, USA) at 25000 rpm for 10 min at 25 °C. In the second step, the emulsions were sonicated using a Sonics Vibra Cell VCX 130 PB sonicator (Sonics & Materials, Inc., Newtown, CT, USA) at 55% amplitude and frequency of 20 kHz for 2 min. The emulsions were named E-R1, E-R2 and E-R3.

2.4 Characterization of the emulsions

The emulsion polydispersity and stability were studied by differential Scanning calorimetry (DSC). The calorimetric analysis was done using a DSC Q1000 (TA Instruments, New Castle, DE, USA). 6-10 mg of emulsion samples were introduced in hermetic pans which in turn were introduced in the furnace of the calorimeter stabilized at 20 °C. Then, the samples were cooled at $3^\circ\text{C}\cdot\text{min}^{-1}$ until reaching -6°C , and then followed by a heating ramp of $5^\circ\text{C}\cdot\text{min}^{-1}$ until a temperature of 25°C was reached.

The micrograph of the were taken using an Olympus BX45 phase contrast microscope (Olympus Optical Co., Ltd., Tokyo, Japan) equipped with a digital camera Moticam 2300 (Motic group Co., Ltd., Xiamen, China).

3 RESULTS AND DISCUSSION

3.1 Characterization the CTAB–SiO₂ aggregates

Different amounts of colloidal silica dispersions (R1, R2 and R3) and CTAB were investigated to tune the hydrophobicity of the nanoparticles. The addition of CTAB and NaCl at constant ionic strength to the colloidal SiO₂ dispersion caused the nanoparticles to flocculate into microsized aggregates. Figure 1a) shows the volume frequency of particle size distribution for fresh solutions R1, R2 and R3 and figure 1b) presents the particle size distribution of the CTAB–SiO₂ aggregates after being sonicated during 2 min. R1 is represented by the higher [CTAB]/[SiO₂] ratio and exhibited a Gaussian distribution with a span ranged between 2.2 and 150 μm. When the ratio decreased, slight deviations from Gaussian distributions occurred by the appearance of shoulders at the high and low particle size ends. The span for R2 varied from 0.5 to 300 μm and it was situated between 0.2 to 300 μm for R3. When the solutions were sonicated, R1 showed a unimodal size distribution skewed towards lower particle sizes with a span ranging from 0.4 to 45 μm. R2 exhibited a bimodal size distribution and a span ranged between 0.15 and 70 μm. Finally R3 presented a multimodal size distribution and a span varying between 0.2 and 120 μm. These results showed that the SiO₂ particles tended to form microsized aggregates due to intra and interparticle attractive forces. After sonication, the particles tended to reorganize again into polydispersed aggregates at a rate that depend on the nature of the attractive forces operating in the solutions.

The zeta potential and pH indicated in Table 1 decreased as the CTAB-SiO₂ ratio in the colloidal dispersions increased. These results showed that CTA⁺ adsorbed on the surface of the particles diminishing the negative charge of the particles and orientating their tail towards the aqueous phase [3]. The formation of hydrophobic bridges between particles and their charge reduction lead to the flocculation of them. Adsorption of CTA⁺ on the particle surface also modifies the wettability of the particle. At low CTAB concentration, the particle

surface is slightly hydrophobic and become highly hydrophobic when a CTAB monolayer is formed. From this statement, it can be admitted that the hydrophobicity of the aggregates followed this order from higher to lower as: $R1 > R2 > R3$.

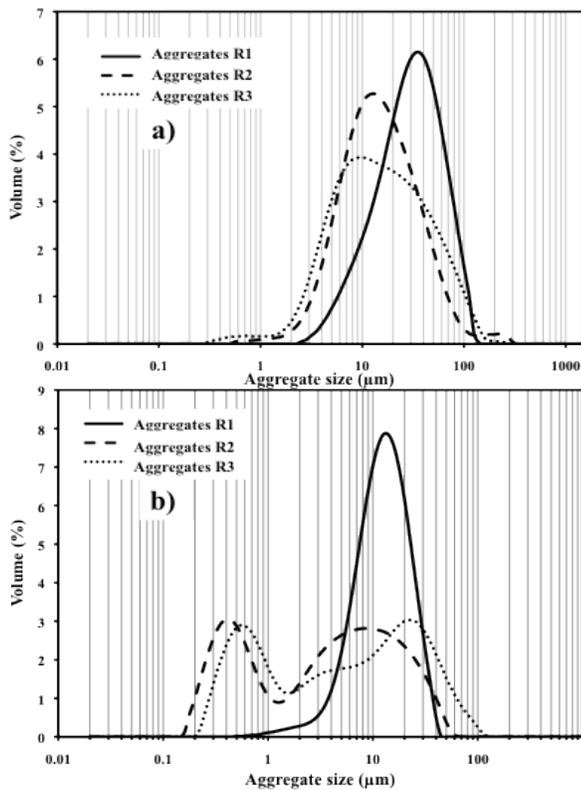


Figure 1: Particle size distribution of the CTAB-SiO₂ aggregates a) fresh solutions and b) after sonication.

3.1 Static viscoelastic properties of the interfacial films

The interfacial creep compliance time profiles of the films and viscoelastic parameters presented in figure 2 indicate that the CTAB-SiO₂ aggregates of solutions R3 and R2 developed highly structured films whose interfacial creep compliance-time behavior decreased with increasing ageing time of the films. The elastic behavior of F-R2 and F-R3 could be related to the cluster size of aggregates and their hydrophobic bridging capability. The compact hydrophobic clusters of solution R1 with relative low surface charge could not form a continuous network at the interface due to sedimentation phenomena limiting their absorption at the interface and for that reason the interfacial creep compliance profile is not presented.

3.2 Characterization of the emulsions

The DSC freezing curves of the freshly prepared emulsions (Day 0) are presented in figure 3. All the emulsions are characterized by deformed bell shape curves at positive temperature which indicate that the emulsions are polydisperse. E-R3 exhibited two crystallization peaks at 4°C and 7°C which overlap. E-R2 was composed of two

crystallization peaks of bell shape at 6.5°C and 8.5°C. E-R1 was predominantly composed of a crystallization peak of bell shape at 9°C together with another crystallization peak of sharp shape at 15.5°C. The crystallization peaks at lower temperatures indicates smaller sized droplets, so that E-R3 presented smaller sized droplets distribution than E-R2 than E-R1. Micrographs of fresh emulsions are also presented in figure 3 and show that E-R1 exhibited larger average droplets size than E-R2 than E-R3. It has been observed that the larger was the mean droplet size of the emulsions the higher was the relative fraction of non-spherical droplets within them. This phenomenon could be attributed to the saturation of the droplet interfaces by the CTAB-SiO₂ aggregates that lead to the formation of solid-like interfacial layer.

All the emulsions were prepared following the same procedure therefore the differences observed in mean droplet size may be imputed to electrical and diffusional factors. From figure 1, one can see that R2 and R3 presented relatively high fraction of smaller aggregates compared to R1, so that when the interface is broken during the emulsifying process, the aggregates of small size diffused and adsorbed at the interface more rapidly than the larger aggregates of R1. From this statement, it can be considered that incipient coalescence proceeded to a much larger extent in E-R1 than in E-R2 and E-R3. Consequently, the average droplet size observed increasing from ratio R3 to R1 could be attributed to the positioning of the aggregates at the droplet interface and due to reduced number of aggregates adsorbed. On the other hand, Binks et al. [4] demonstrated that the average droplet size of emulsions increases with the particle diameter. As it has been observed that the disrupted aggregates tend to reorganize again in solutions after sonication therefore it can be supposed that this phenomenon could also occur at the droplet interface. Despite R2 contains aggregates of smaller size aggregates than R3, they adsorbed at the interface and reorganized themselves due to their higher hydrophobic bridging capabilities thus forming bigger cluster and positioning differently than those of R3 at the interface. From this statement it is understandable that R1 lead to the formation of an emulsion with the higher average droplet size.

3.3 Emulsion stability

Figure 3 also presents the DSC freezing curves obtained over 57 days. E-R1 and E-R2 exhibited similar profiles at different ageing times indicating that the droplet size did not really change and thus the emulsions were very stable.

Contrarily, E-R3 presented changes during times. The crystallization peaks of the droplets at 4.5°C displayed at $t = 0$ day shifted towards higher temperatures as the ageing time increased to finally gives rise to the presence of only one crystallization peak at 8.0°C at day 57. E-R3 evolved into a more stable emulsion displaying a more homogeneous but larger mean droplet size. This phenomenon could be attributed to a reorganization of the CTAB-SiO₂ aggregates at the droplet interface over time to

form bigger clusters. Therefore the area covered by the aggregates decreased leading to the formation of vacant holes in the interfacial layer [5]. Consequently, fusion of droplets should occur to reduce the vacancy area in the aggregate layer and this process ended when an aggregate plateau concentration at the interface droplet was reached leading to the formation of droplets with larger droplet size.

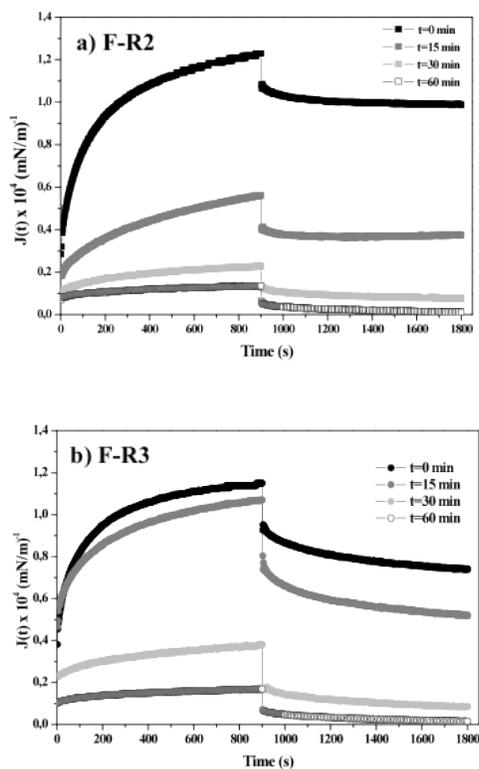


Figure 2: Creep compliance–time curves for the CTAB–SiO₂–NaCl interfacial films at different aging times: a) F-R2, b) F-R3.

4 CONCLUSION

Different amounts of colloidal silica dispersions (R1, R2 and R3) and CTAB were investigated to tune the hydrophobicity of the nanoparticles. The addition of CTAB and NaCl at constant ionic strength to the colloidal SiO₂ dispersion caused the nanoparticles to flocculate into microsized aggregates. The emulsions exhibited long-term stability against coalescence despite having polydisperse droplet sizes. The larger mean droplet size could be attributed to the diameter of the CTAB–SiO₂ aggregates and their position at the interface. The non-spherical shape of the droplets could be attributed to the solid-like behavior of the interfacial films that may be related to the capability of CTAB–SiO₂ aggregates to form hydrophobic bridges. The emulsion prepared with the lower [CTAB]–[SiO₂] ratio, R3, exhibited changes in the average droplet size with aging time, attributed to a reorganization of the aggregates at the interface into larger clusters. It is note worthy this

work also demonstrates that interfacial shear rheology is an available technique to study viscoelastic properties of nanoparticle-surfactant structured films as well as calorimetric analysis represents a tool for determining long-term stability of emulsions in short time.

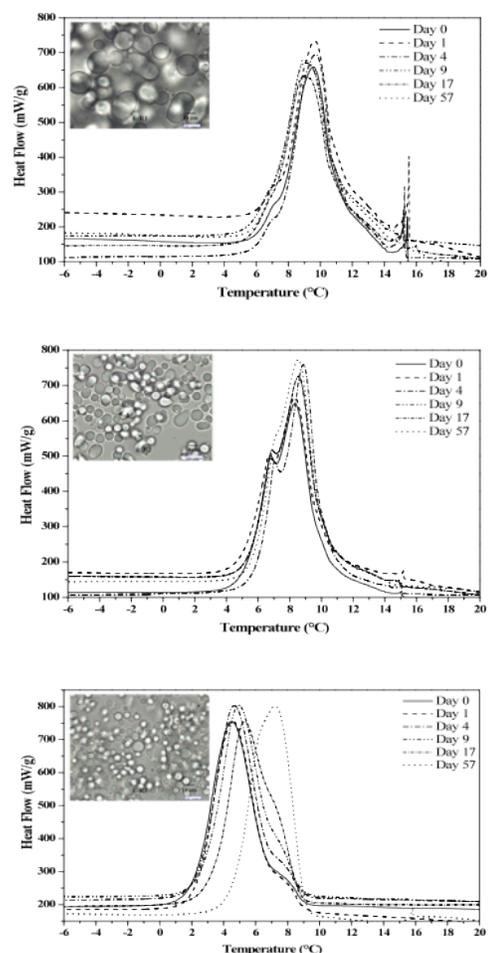


Figure 3: Evolution of the DSC freezing curves and micrographs for the H/W emulsions: a) E-R1, b) E-R2, and c) E-R3.

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