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Aqueous foams and emulsions stabilized by mixtures of silica nanoparticles and surfactants: A state-of-the-art review

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ABSTRACT

In the last years, mixtures of silica nanoparticles and surfactants have been widely and successfully used to stabilize a multiplicity of aqueous foams and emulsions with current and potential applications in the engineering processes. The physicochemical properties and large-scale industrial production of silica nanoparticles, as well as the practical and cheap methods offered by surfactants to modify the nanoparticles' wettability, are the main reasons for the silica nanoparticle-surfactant pair to be an effective combination on the stabilization of both aqueous foams and emulsions. This state-of-the-art review aims to offer a well-defined picture of the contemporary research on foams and emulsions (oil-in-water, water-in-oil, and the particular case of the bicontinuous ones) stabilized by mixtures of silica nanoparticles and surfactants (cationic, anionic, nonionic, and zwitterionic) featuring the top results and outlining future research in the area. Attention is paid to the processes and materials where the foams and emulsions discussed are present. The function of silica nanoparticles-surfactants synergy on stabilizing foams and emulsions is also discussed.

1. Introduction

Aqueous foams and emulsions are both dispersions that are essential in chemical engineering. Whereas aqueous foams are dispersions of gas bubbles in an aqueous phase, emulsions are dispersions of oil droplets in water (direct or O/W emulsions) or water droplets in oil (inverse or W/O emulsions). Both systems are thermodynamically unstable and evolve via three mechanisms: drainage occurs in the case of foams, while creaming (droplet rising) or sedimentation (droplet setting) in the case of emulsions, both due to the effect of gravity; coarsening takes place in foams or Ostwald ripening in emulsions, owing to the transfer of gas (in the case of foams) or liquid (in the case of emulsions) from smaller bubbles (droplets) to the bigger ones, because of pressure differences due to the curvature; and finally coalescence in bubbles/droplets, that happens as the film between them ruptures.

The industrial applications of foams and emulsions are numerous, mainly in industrial processes related to food, cosmetics, pharmacy, enhanced oil recovery (EOR), and synthesis of macroporous materials [1,2]. However, the metastability of both systems represents a challenge for their optimal formulation and handling. Traditionally, foams and emulsions are stabilized by surfactants, but their rapid adsorption and desorption at fluid interfaces do not allow them to produce highly stable systems [3]. A successful approach to stabilize dispersed systems was first conceived more than one hundred years ago by Ramsden and Pickering, who explored how particles could stabilize bubbles [4] and oil droplets [5]. For this reason, particle-stabilized emulsions (foams) are called Pickering emulsions (foams). Although the research on stabilizing foams and emulsions by particles started a century ago, systematic studies trying to elucidate their stabilization mechanism have been developed in the last two decades. The great effectivity of particles in stabilizing foams and emulsions lies in their high adsorption energy at fluid interfaces. They irreversibly adsorb at liquid-liquid and liquid-gas interfaces. Once the particles are anchored at an interface, droplets and bubbles get a character of 'solid-like armor' against coarsening and coalescence processes, which leads the foams and emulsions to survive high lifetimes [6–9]. Particles can also slow down drainage in foams because they increase bulk viscosity, aggregate in the foam liquid channels (Plateau borders), or act as gelling agents [10–12]. In emulsions, particles can form networks between droplets or aggregate in the continuous phase, which increases the emulsion stability to creaming (sedimentation) [13,14].

Silica nanoparticles (SiO_2 NPs) have been extensively used to stabilize foams and emulsions because of their surface chemistry, thermal stability, large-scale industrial production, and low cost [15,16]. The critical parameter for SiO_2 NPs in the elaboration and stabilization of foams and emulsion is their hydrophilic or hydrophobic character, a property related to wettability and the three-phase contact angle θ (measured with respect to water, see Fig. 1a). It has been theoretically shown

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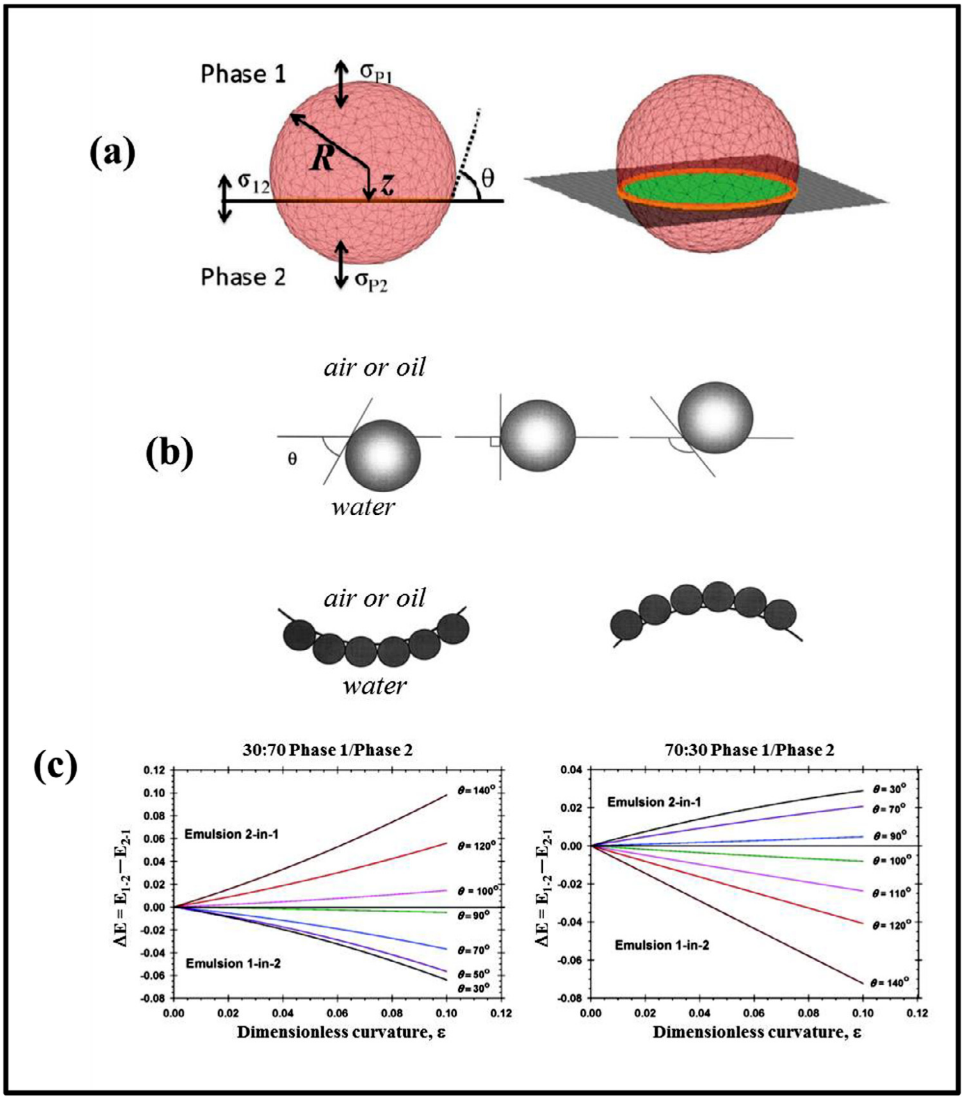


Fig. 1. (a) Schematic representation of a spherical particle at a fluid interface. Left: 2D cross-section of the position of the particle at the interface. Right: 3D representation of the area of the fluid interface that is removed upon adsorption of the colloidal particle (green area) and the three-phase contact line that contributes to line tension effects (orange line). To interpret color in this figure legend, the reader is referred to the web version of this article. (Reproduced with permission [43] Copyright 2019, The Royal Society of Chemistry). (b) Top: location of a small spherical particle at a planar fluid-water interface for a contact angle (θ) less than 90° (left), equal to 90° (center), and larger than 90° (right). The contact angle is measured through the aqueous phase as a reference. Bottom: Corresponding probable positioning of particles at a curved fluid-water interface. Left: for $\theta < 90^\circ$ solid stabilized aqueous foams or O/W emulsions may be formed. Right: for $\theta > 90^\circ$ solid stabilized aerosols or W/O emulsions may be formed. (Reproduced with permission [3] Copyright 2002, Elsevier Science Ltd.). (c) Plot of ΔE vs the dimensionless curvature $\varepsilon = R/R_{12}$, of the formed drops. Left $\varphi_1 = 0.3$; right $\varphi_1 = 0.7$. The different curves correspond to different values of the contact angles, θ; $\varphi_a = 0.9$ is fixed. $\Delta E < 0$ and $\Delta E > 0$ correspond to the formation of emulsions 1-in-2 and 2-in-1, respectively. (Adapted with permission [53] Copyright 2005, American Chemical Society).

that to elaborate stable foams, the particle contact angle should be between 50° and 90° [17]; however, after reviewing the role of particles in stabilizing foams, Hunter et al. [18], pointed out that the optimal particle contact angle occurred between 60 and 70° On the other hand, the type of emulsion obtained somehow depends on the particle contact angle. As a general rule, hydrophilic particles ($\theta < 90^\circ$) tend to form O/W emulsions, whereas for hydrophobic particles ($\theta > 90^\circ$) W/O emulsions are more probably created [19]. Nevertheless, this rule is far from being so easy, as we will discuss in Section 2.2; several factors influence the formation of O/W or W/O emulsions besides the contact angle, as the volume fractions of both aqueous and oleous phases, and bending energy. Moreover, emulsions elaborated with either too hydrophilic or hydrophobic SiO_2 NPs are not stable against coalescence, since nanoparticles in these conditions do not strongly adsorb at the liquid-liquid interface [20–22]. These features for both dispersed systems confirm that, for obtaining stable foams and emulsions, nanoparticles must present a specific wettability.

In their natural form, SiO_2 NPs have a hydrophilic character. SiO_2 NPs of 20–30 nm size at the air-water interface showed a contact angle of approximately 15°, measured by immersion tests [23]. Kostakis et al. [24] measured the contact angle of pure water droplets on a flat silica surface made by pressing silica nanoparticles with a diameter of 20 nm, obtaining a value near 20°. These values suggest that to attaining an intermediate wettability (contact angle), SiO_2 NPs require surface modification to become more hydrophobic. A common pathway to increase silica nanoparticles' hydrophobicity is to treat their surface generally with dichlorodimethylsilane [25,26], although other silane compounds are sometimes used [27–29]. The degree of hydrophobization will depend on the content of silane grafted on the silica surface through a silanization reaction. However, the main disadvantages of silanization are the generation of subproducts and the use of solvents during the process [30,31], requiring operations of separation after the reaction, which leads to higher costs and invested time.

A money-saving and less laborious technique to adjust the hydrophobicity of SiO_2 NPs based on the in situ modification of the nanoparticles surface using surfactants has been developed in the last decade. Due to different interactions, surfactant molecules adsorb on the nanoparticle surface, changing its wettability; thus, the particle's hydrophobic character will depend on the amount of surfactant adsorbed [32,33]. Furthermore, no additional solvents are required. Diverse processes in chemical engineering may take advantage of foams and emulsions, which are stabilized by the combined effect of nanoparticles and surfactants (synergy) to achieve optimal results in their operation: EOR [34,35], fabrication of macroporous materials [36,37], and formulation of "food-grade" products [38,39] are some of them. This review emerges based on existing and potential applications of foams and emulsions stabilized by SiO_2 NPs-surfactants mixtures. Although a couple of reviews on the topic have been recently published, they covered reports on foams [40] and emulsions [41] stabilized by different types of nanoparticles.

Then, studies on stabilization of SiO_2 NPs-surfactants mixtures in foams and emulsions were not fully addressed.

Rather than focusing on stabilization mechanisms, this manuscript offers a picture of the contemporary research on foams and emulsions stabilized by SiO_2 NPs (mean diameter $\leq$ 100 nm)-surfactant assemblings, highlighting the central results, and glimpsing the directions for oncoming investigations. We first describe the role of particles and SiO_2 NPs-surfactants mixtures in the stabilization of foams and emulsions. Next, we analyze diverse foams and emulsions (O/W and W/O) stabilized by different mixtures of SiO_2 NPs and surfactants, to discuss later the case of the bicontinuous emulsions. The reports are organized into different engineering fields where both, the examined foams and emulsions, have or would possibly have an application. We conclude by providing some possible directions for future investigations on this topic.

2. Foams and emulsions stabilized by particles: some remarks on their formation and stabilization

2.1. Stabilization of flat fluid interfaces with particles

The way particles stabilize foams and emulsions is associated with particle detachment energy from fluid interfaces, which is large compared to surfactant molecules. The detachment energy of spherical particles considering the particle is sufficiently small to neglect gravity effects (Bond number << 1) is given by [3,18]:

$$E = \pi R^2 \sigma_{12} (1 \pm \cos\theta)^2, \tag{1}$$

R is the particle's radius and σ_{12} is the interfacial/surface tension of the liquid-liquid or liquid-gas interface (Fig. 1a). The sign inside the bracket will be negative if the particle is removed into the aqueous phase, or positive if removed into the oil or air phase. The higher the detachment energy, the stronger the particle is held at the interface in contraposition with surfactant molecules, which adsorb and desorb on a fast timescale [3].

At the nanoscale, dissension arises on the effects of line tension in Eq. (1), as the line tension (see Fig. 1a right) term indicates the excess of free energy per unit length of a three-phase contact line [42,43]. By analyzing results from optical experiments, de Gennes et al. [44] stated the line tension had no scientific support and considered it a consequence of experimental artifacts; however, these authors suggested using non-optical techniques for the estimation of line tension. In fact, through scanning force microscopy experiments, the line tension values obtained for micrometric droplets on a silicon wafer surface were in the range from 10^{-11} to 10^{-10} J/m [45]. On the other hand, some efforts to identify the effects of the line tension on particles at interfaces have been carried out [46, 47]. Nonetheless, due to restrictions to get experimental information on line tension when working at the nanoscale, simulations are useful tools [48–50]. A density functional theory study performed for nanoparticles at a vapor-liquid interface pointed out a negligible line tension effect for contact angles between 60° and 120°, but a remarkable influence for contact angles greater than 120° or less than 60° [48]. Although the literature on the line tension is vast, the theme remains under discussion.

2.2. Link between particle contact angle and the formation of foams and emulsions. Spherical liquid-liquid interfaces

Particle wettability strongly influences the type of dispersion obtained. When $\theta < 90^\circ$, most of the particle surface is wetted by the aqueous phase (hydrophilic character), and for $\theta > 90^\circ$, the particle is mostly in contact with air (gas) or the oil phase (hydrophobic character), as observed in Fig. 1b. Foams are generally stabilized with hydrophilic particles since it is known that particles with $\theta > 90^\circ$ induce dewetting behavior and film rupture [51], but they may stabilize water-in-air dispersions known as liquid marbles [52]. In the case of emulsions, the criterion to create and stabilize a certain type of emulsion (O/W or W/O) goes beyond the influence of the particle contact angle, as will be described in the following paragraphs.

Microemulsions are thermodynamically stable and form spontaneously. However, the formation of Pickering emulsions demands an input of energy. It is needed to break the disperse phase down into small drops. Afterward, the solid particles adsorb on the newly formed oil-water interface, accompanied by a gain of adsorption energy. Consequently, the produced emulsion can be very stable due to the adsorbed particles' steric drop-drop repulsion. From a thermodynamic viewpoint, the Pickering emulsion is metastable. Nonetheless, a thermodynamic treatment can be given to understand the variables that determine its formation supposing the following conditions: the particles adsorb very fast at the oil-water interface; once adsorbed, the particles do not desorb from the surface of the emulsion drops; the emulsion reaches a metastable thermodynamic equilibrium in a local minimum of free energy. One additional assumption is that the drops are spherical.

When a two-phase (oil/water) system is subjected to homogenization, both the direct and reverse emulsions can be simultaneously formed in different spatial domains of the system. However, only that which is more stable survives, that is the state of lower free energy. In Pickering emulsions, the gain of surface energy upon particle adsorption is usually much greater than the emulsification's entropy effects. To evaluate the emulsification energy, we follow Kralchevsky et al. [53]. We will consider that the solid particles are initially dispersed in phase 2 (aqueous phase). The dispersion of phase 1 (oil phase) into phase 2 will be named "emulsion 1-in-2″. It corresponds to the Bancroft rule (oil-in-water) since particles are in the continuous phase, while the reverse emulsion (water-in-oil) will be "emulsion 2-in-1″. In general, we will consider the whole interval of $0 < \theta < 180^\circ$. The breakage of a given volume of liquid into drops leads to an enlargement of the surface area and, consequently, the adsorption of additional solid particles. The volumes of phases 1 and 2 and the total number of particles are assumed to be constant during emulsification. For simplicity, it is supposed that the emulsion drops are monodisperse. The difference between the (interfacial) energy for the formation of the emulsions 1-in-2 (E_{1-2}) and 2-in-1 (E_{2-1}) is given for the following formulas:

$$\Delta U = \left(\frac{3\sigma_{12}}{R}\right)\Delta E = \left(\frac{3\sigma_{12}}{R}\right)(E_{1-2} - E_{2-1}). \tag{2}$$

Where ΔE corresponds to a series in ε, where the most important term is

$$\Delta E = \varepsilon(2\varphi_1 - 1)(1 - \varphi_a b) + \varepsilon^2 \varphi_a \left[\{(2 + \cos\theta)b + 4\varphi_1 - 4\}(1 - \varphi_a b) - 2b\cos\theta\right]. \tag{3}$$

In Eq. (3), $\varepsilon = {}^{R}/_{R_{12}} << 1$ is the particle to drop radius ratio, σ_{12} is the interfacial tension, $b = (1 - \cos\theta)^2$, $\varphi_2 = 1 - \varphi_1$ corresponds to the volume fraction of phase 2 in the emulsion, as well as φ_1 is the volume fraction of phase 1, and φ_a is the area fraction occupied by the adsorbed particles, which is limited by the maximum particle area fraction, *i. e.*, $0 < \varphi_a < 0.907$. This formula is not particularly simple, with a complex dependence on contact angle and volume fraction that gives rise to different situations observed experimentally. ΔE provides a thermodynamic guide about which emulsion will form upon agitation (Fig. 1c). For ΔE (= $E_{1-2} - E_{2-1}$) < 0, emulsion 1-in-2 will be formed, on the contrary when ΔE (= $E_{1-2} - E_{2-1}$) > 0, emulsion 2-in-1 will be formed. Fig. 1c presents an example with two diagrams of ΔE vs. the dimensionless drop curvature, ε, for several values of the contact angle θ and two-phase volume fractions, $\varphi_1 = 0.3$ and $\varphi_1 = 0.7$, as presented in [53]. In a volume fraction of $\varphi_1 = 0.3$ and for particles with $\theta \leq 90^\circ$ (hydrophilic), emulsions 1-in-2 will be formed ($\Delta E < 0$). On the contrary, for the same particles with $\theta \leq 90^\circ$, since $\Delta E < 0$ emulsions 2-in-1 will be formed when the volume fraction φ_1 is larger than φ_2. This phase inversion happens at volume fractions φ = 50:50, owing to the change in the sign of the first term in Eq. (3), proportional to $(\varphi_{1\,-}\,\varphi_2)$. In other words, for $\varphi_1 > 0.5$, the formation of the emulsion 2-in-1 becomes more gainful in terms of free energy. This calculation explains

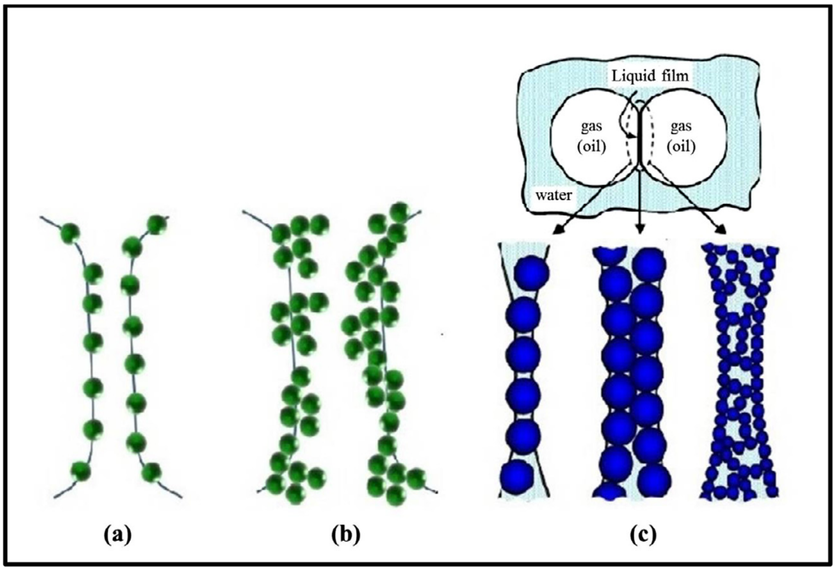


Fig. 2. Sketch of fluid interfaces stabilization by particles adsorbed as (a) monolayer and (b) multilayers. (Adapted with permission [54] Copyright 2014, Elsevier Masson SAS). (c) Scheme of the possible mechanisms of liquid film stabilization. Left: monolayer of bridging particles. Center: bilayer of close-packed particles. Right: a network of particle aggregates inside the film. (Reproduced with permission [67] Copyright 2014, Elsevier Ltd.).

the sudden phase inversion changes upon variation of solvent volume fractions observed in Pickering emulsions. However, it is important to highlight that, in experiments, the observations may be different from the theoretical predictions due to kinetic factors as particle adsorption rate, particle desorption, and metastability [53]. We must also consider that surfactants, even at low concentrations, can modify the adsorbed particles' contact angle, thus influencing the type and stability of the formed emulsion.

2.3. *Consequences of particles at fluid interfaces on the stabilization of foams and emulsions*

When particles attach at fluid interfaces as monolayers (Fig. 2a) or aggregates (Fig. 2b) [54], the interfacial dilational viscoelasticity increases, i.e., the interfacial dynamic resistance to changes in area (extension or contraction) [55,56] augments, and so does foam/emulsion stability [57,58]. Moreover, the solid-like character of particle-stabilized interfaces may trigger the apparition of polymorphous droplets or bubbles [59,60].

Particles anchored at interfaces stabilize foam and emulsions by forming a steric barrier against coarsening/Ostwald ripening and coalescence. The particle shell around bubbles/droplets slows down gas/liquid diffusion from the smaller bubbles/droplets to the bigger ones. Indeed, to halt coarsening/Ostwald ripening and coalescence, bubbles/droplets require a particular particle surface coverage [6–8,61,62]. Furthermore, particles influence the maximum capillary pressure of coalescence (P_c^{max}) in bubbles and droplets. Recalling that the capillary pressure (P_c) is the difference between the pressure inside a bubble/droplet and the pressure inside the interfilm liquid [63], high P_c^{max} values mean the liquid film is capable of resisting higher pressures, that is to say, the system's stability is enhanced. Kaptay [64] extended the method developed by Visschers et al. [65] to formulate the following equation, which characterizes the effect of a single layer of particles residing in a bubble-bubble (droplet–droplet) interfilm on P_c^{max}:

$$P_c^{\max} = \pm p \frac{2\sigma_{12}}{R} \cos\theta. \tag{4}$$

The sign "+", corresponds to O/W emulsions and foams, and the sign "−", to the case of W/O emulsions, whereas p is a packing parameter. From this expression, smaller particles will be more favorable for coalescence suppression in terms of maximum capillary pressure, of course, depending on the packing parameter. Moreover, it is possible to analyze the combined effect of particle contact angle maximum capillary pressure and detachment energy expressions to determine particle contact angles that offer the best foam/emulsion stability [64].

When particles are located between two interfaces (inside the films), different scenarios are observed (Fig. 2c). Bridging monolayers and particle bilayers preventing bubble/droplet coalescence [66,67]. When particle concentration increases, a network of particle aggregates (gel-like) is structured inside the film, which hinders drainage (creaming in emulsions) and coalescence [67,68]. The way particles organize at interfaces and stabilize foams or emulsions are governed by particle-particle interactions: repulsive or attractive from electrostatic origin, or due to capillarity [69–72], which can be modulated by the presence of salt or surfactants in the solutions [73,74].

3. Interactions between silica nanoparticles and surfactants: effect on the stability of foams and emulsions

Mixtures of SiO_2 NPs and surfactants have been broadly employed to elaborate and stabilize foams and emulsions; in fact, these studies are the focus of the current state-of-the-art review. The effects of particles on the stabilization of foams and emulsions discussed in section 2 (detachment energy, maximum capillary pressure, and particle structuration inside films), also apply for SiO_2 NPs in the presence of surfactants. Therefore, it is relevant to mention the main interactions between SiO_2 NPs and the different types of surfactants to better understand their combined effect on foams and emulsions stabilization. The following analysis briefly describes the surfactant effect on the nanoparticle contact angle, and how SiO_2 NPs-surfactants mixtures influence interfacial/surface tension. Both particle contact angle and interfacial/surface tension are parameters that impact the detachment energy equation (Eq. (1)).

In general, unmodified SiO_2 NPs are found in mediums whose pH values are above the silica isoelectric point (around 2). At those pH values, silica nanoparticles are negatively charged as their surface is covered by silanol groups [75] and are too hydrophilic to stabilize foams and emulsions alone (the nanoparticle detachment energy is low). When mixed with cationic surfactants, the wettability of SiO_2 NPs is modified as surfactant molecules are adsorbed on silica surfaces due to electrostatic interaction. As surfactant monomers are adsorbed on nanoparticles surface, their hydrocarbon chains are exposed to the aqueous medium, which increases the hydrophobic character of nanoparticles and makes them able to stronger attach at air-liquid and liquid-liquid interfaces [76–78], and consequently to halt coarsening/ripening and coalescence processes [10]. If additional surfactant adsorption occurs, a surfactant bilayer is formed through hydrophobic chain-chain interaction, exposing the polar heads to the aqueous medium, turning nanoparticles hydrophilic again and disadvantageous for foams and emulsions stabilization [32,79,80]. A representation of cationic surfactant molecules

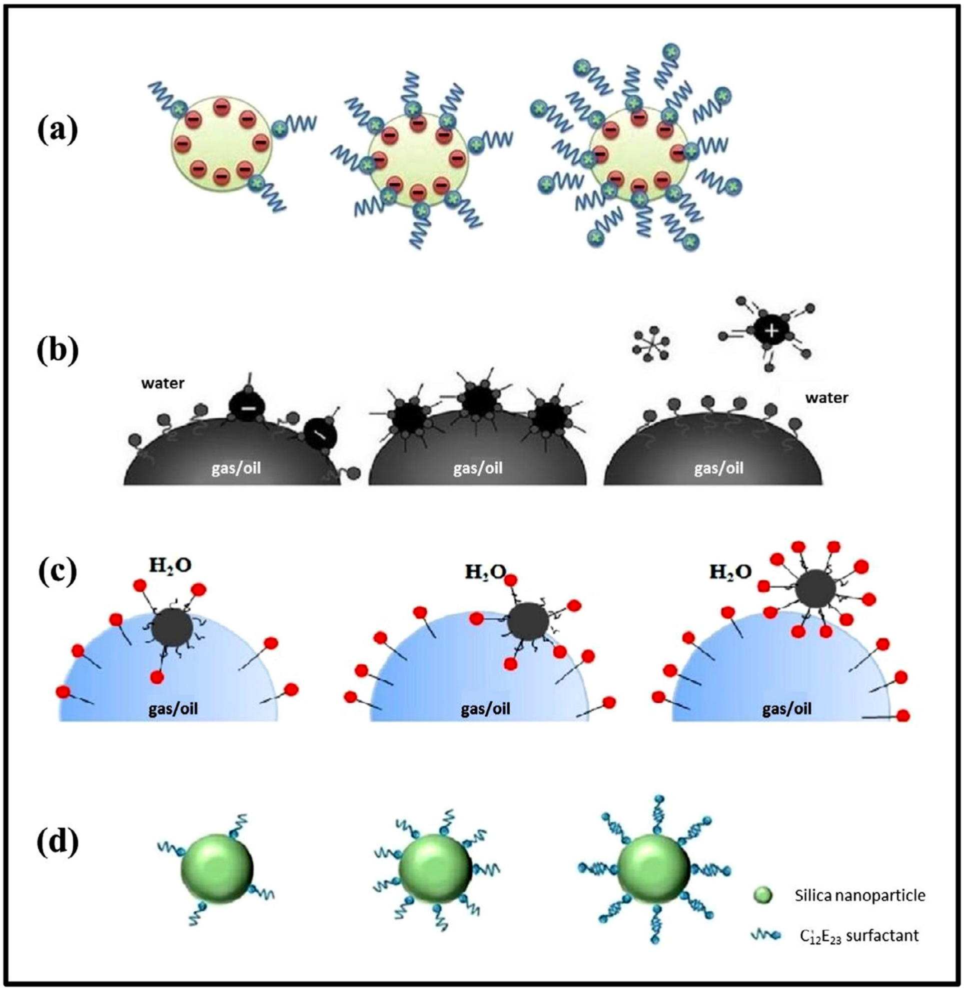


Fig. 3. (a) Modification of the hydrophobicity of a negatively charged particle due to the interactions with a cationic surfactant. (Reproduced with permission [32] Copyright 2012, The Royal Society of Chemistry) (b) Representation of the bubble/oil droplet stabilization by the silica particle-cationic surfactant synergy at high pH. Left: at low surfactant concentration, a small amount of particles partially covered with surfactant is attached at interfaces, which mainly contain surfactant molecules. Bubbles/droplets are rather unstable. Center: at intermediate surfactant concentrations, bubbles/droplets are stable since their surfaces are covered with particles onto which a surfactant monolayer has been adsorbed, rendering them hydrophobic. Right: at high surfactant concentrations, very unstable bubbles/droplets contain an adsorbed surfactant layer; cationic particles coated with surfactant bilayers and surfactant micelles remain dispersed in the aqueous phase. (Adapted with permission [10] Copyright 2008, The Royal Society of Chemistry). (c) Positions of hydrophobic SiO_2 NPs relative to the interface. As the sodium dodecyl sulfate (SDS) concentration increases (from left to right) at a fixed nanoparticle concentration, the hydrophobic nanoparticles are transported from the gas/oil phase to the aqueous phase due to SDS adsorption on the surface of nanoparticles. (Adapted with permission [126] Copyright 2016, American Chemical Society). (d) Adsorption of the nonionic surfactant $C_{12}E_{23}$ on a silica nanoparticle. The surfactant concentration increases from left to right. (Adapted with permission [99] Copyright 2019, American Chemical Society).

adsorption on SiO_2 NPs is shown in Fig. 3a, whereas Fig. 3b depicts the bubble/droplet stabilization through this synergy.

Mixtures of cetyltrimethylammonium bromide (CTAB), which is one of the cationic surfactants most used for foams and emulsions elaboration, and SiO_2 NPs show higher surface/interfacial tension values compared to those obtained for just surfactant solutions [14,76,81] since surfactant adsorption onto the SiO_2 NPs causes free surfactant depletion (surfactant is sequestered). Nevertheless, the opposite tendency has been reported, especially at low surfactant concentrations [13,61,82]. Moreover, the surfactant tail length has an effect on the surface tension value of C_nTAB/SiO_2 NPs complexes [83]. Particle flocculation can occur when cationic surfactant-covered nanoparticles get closer as electrostatic repulsion is reduced. Interestingly, emulsion and foam stabilization is enhanced when particles are flocculated since flocs may adsorb at the interfaces, providing resistance to coalescence through increasing bulk viscosity and diminishing drainage/creaming rate [10,11,13,14].

The electrostatic interaction principle observed in negatively charged SiO_2 NPs-cationic surfactants synergy can be generalized for other SiO_2 NPs-surfactants systems. Emulsions elaborated with mixtures of alumina-coated SiO_2 NPs (positively charged) and an anionic surfactant showed their highest stability against creaming and coalescence when elaborated with the most flocculated dispersions, suggesting that oppositely charged SiO_2 NPs-surfactants combinations offer the same stabilization mechanism in foams and emulsions [84,85].

Stabilization of foams combining negatively charged SiO_2 NPs and anionic surfactants has been discussed in terms of particle entrapment in liquid channels, which contributes to slow down drainage [86], and to increment the maximum capillary pressure of coalescence [87]. In emulsions, the resistance to droplet coalescence was linked to liquid-liquid interfaces stabilized by both surfactants and a considerably high amount of nanoparticles [88,89], as well as a viscosity increase caused by the formation of a particle network [89]. When negatively charged hydrophilic SiO_2 NPs are mixed with anionic surfactants, a reduction in the interfacial/surface tension is observed due to the electrostatic repulsive interactions that promote the surfactant adsorption at the oil-water interface and gas-water surface [81,88,90,91]. Since a part of an anionic surfactant can be adsorbed onto the negatively charged silica surface, Ahualli et al. [81] referred to these systems as supercharged. Interestingly, it was recently demonstrated that the surface activity observed in negatively charged SiO_2 NPs-anionic surfactants mixtures was mainly a consequence of a change in the system's ionic strength [92].

Regarding hydrophobic SiO_2 NPs, hydrophobic interactions promote the adsorption of anionic surfactant molecules on the silica surface [93]. As shown in Fig. 3c, when increasing anionic surfactant concentration, surfactant tails adsorb on silica nanoparticles. Surfactant head groups are exposed to the aqueous medium, which causes a decrease in the hydrophobic character of nanoparticles and their gradual displacement towards the aqueous phase. Although further exploration with other anionic surfactants is required, studies report mixtures of partially hydrophobic SiO_2 NPs and sodium dodecyl sulfate (SDS) at diluted concentrations (below the critical micelle concentration, CMC) that present lower surface/interfacial tension values compared to SDS solutions [94–96]. In contrast, at higher surfactant concentrations, the opposite trend is found [94,95]. The explanation of this behavior was given as follows: at low SDS concentrations, the adsorption of both surfactant and nanoparticles-surfactant entities at the surface/interface decreases surface/interfacial tension; but when more SDS is added, it adsorbs onto the nanoparticles, which causes surfactant depletion at the fluid interface and an increase in the interfacial tension [95,96]. As expected, foams and emulsions elaborated with dispersions of anionic surfactants and partially hydrophobic SiO_2 NPs are stabilized due to the formation of armors on the bubble/droplets interfaces that inhibit coalescence and coarsening [95,97,98].

Concerning nonionic surfactants, it is known that polyethylene oxide (PEO)-based surfactants adsorb on SiO_2 NPs surface through hydrogen bonding with the silanol groups [99,100]. As the surfactant concentration increases, a monolayer on the silica nanoparticle's surface is formed; in this configuration, the surfactant molecules' hydrophobic region is exposed to the aqueous phase, increasing the hydrophobicity of the nanoparticle. At higher concentrations, a surfactant bilayer is formed (SiO_2 NPs become hydrophilic again) [99,101], and the presence of micellar aggregates on the silica surface is also claimed [102,103]. The different stages of PEO-based surfactant adsorption onto SiO_2 NPs are shown in Fig. 3d.

The effect of the nonionic surfactant-SiO_2 NPs synergy on interfacial/surface tension is not well established. While it is argued that these mixtures induce an insignificant decrease or no change in the interfacial/surface tension compared to pure surfactant solutions [90], an increase [82,104] and decrease are also reported [81]. Thus the interfacial/surface tension trend in the presence of nonionic surfactants-SiO_2 NPs seems to depend on the system itself. The SiO_2 NPs-nonionic surfactant synergy positively impacts foam stability by inducing the formation of nanoparticle flocs [33,105], increasing surface elasticity [33,99,105], and rising bulk viscosity [99]. Similarly, emulsions exhibited higher stability in the presence of particle flocs induced by the nonionic surfactant, structures that diminish droplet coalescence and decelerate creaming [104,106].

The synergy cases between SiO_2 NPs and surfactants presented in the preceding paragraphs show how meticulously the selection of both the type of surfactant and the surface chemistry of the SiO_2 NPs should be to reach the expectations on foams and emulsions stabilization. Under this context, diverse silica nanoparticle-surfactant pairs have been explored to stabilize foams and emulsions with current and plausible applications in engineering processes, as will be discussed in the next sections.

4. Literature review of SiO_2 nanoparticles-surfactants foams in different research fields

4.1. Enhanced oil recovery (EOR)

Enhanced oil recovery is one chemical engineering process that has taken advantage of studies on foams. Injection of foams in petroleum reservoirs attracted attention in 1958, when Bond & Holbrook [107] proposed this technique for EOR operations, offering a solution for the low sweep efficiency of gas injection procedures. Foam presents a larger apparent viscosity than that of the gas, allowing better control of viscous fingering and improving oil recovery [108]. Furthermore, in porous media, foams divert from high-permeability layers to those with a lower one, increasing the sweep efficiency [109–111]. However, for a correct implementation in EOR, foams require maximum stability in the reservoirs, an issue that has been studied from different perspectives. As described in this review, foams elaborated with mixtures of silica nanoparticles and surfactants present outstanding stability, and, for this reason, their presence in petroleum recovery research is significant.

4.1.1. Silica nanoparticles and cationic surfactants. Studies with zwitterionic and short compounds

Different mixtures of SiO_2 NPs with cationic surfactants have been reported to pursue effective oil recovery techniques. A study was conducted where the synergy between hydrophilic SiO_2 NPs and the cationic surfactant ethyl hexadecyl dimethyl ammonium bromide ($C_{20}H_{44}BrN$) enhanced the lifetime of carbon dioxide (CO_2) foams generated with the Ross-Miles method [112]. Dynamic analysis of these foams showed an increase in pressure drop and foam viscosity, and a decrease in mobility, which is positive for CO_2 injection processes. Furthermore, flooding experiments in porous media carried out by Li et al. [113] provided enough evidence to consider the implementation of CO_2 foams stabilized by CTAB-SiO_2 NPs in reservoir flooding. On the other hand, results from sand pack experiments were performed with nitrogen (N_2) foams, whose air-water interfaces were covered by hydrophilic SiO_2 NPs-dodecyltrimethylammonium bromide (DTAB), indicating that the nanoparticle armor around bubbles aided foams to present good stability in porous media and injection stages [114].

Not only cationic single-tailed surfactants have been explored. An investigation performed by Pal et al. [115] exposed that air foams whose interfaces were covered by the gemini surfactant N, N′-bis(dimethyl tetradecyl)−1,6-hexanediammonium bromide (14–6–14 GS), and SiO_2 NPs are suitable systems for EOR applications thanks to their great stability, rheological properties, and propitious wettability behavior on sandstone rock specimens. In another report, foams elaborated with mixtures of the gemini surfactant ethanediyl-α,ω-bis(tetradecyl dimethyl ammonium bromide) (14–2–14) and hydrophilic SiO_2 NPs were more stable than foams stabilized by the synergy between SiO_2 NPs and the corresponding surfactant monomer, tetradecyltrimethylammonium bromide (C_{14}TABr) [116]. However, further foam characterization and flooding experiments are necessary to propose the synergistic effect between these gemini surfactants and SiO_2 NPs as advantageous in petroleum recovery processes.

Comparisons between mixtures of SiO_2 NPs with different types of surfactants have been performed in the quest to find an optimal foam with potential applications in oil recovery. In one report, the synergy between SiO_2 NPs and the ionic surfactant CTAB or SDS was evaluated in terms of static foam stability and flow in a Hele-Shaw cell, finding that static experiments cannot provide enough information about foam flow behavior in the presence of oil [117]. Data on foam flow showed that CTAB-SiO_2 NPs foams, which are oppositely charged to the silica nanoparticles, are more suitable in oil recovery processes than those stabilized by SDS-SiO_2 NPs (like-charged) since the mobility of the first ones is lower in the presence of a hydrocarbon. It was also reported that, at an elevated temperature (80 °C), the stability of air foams containing hydrophilic SiO_2 NPs and a cationic surfactant was higher than those containing anionic or nonionic surfactants, mainly due to electrostatic interaction between SiO_2 NPs and cationic surfactant, and aggregation phenomena [118].

Mixtures of zwitterionic surfactants and SiO_2 NPs have also attracted attention to stabilizing foams for EOR purposes. In a study reported by Worthen et al. [119], carbon dioxide foams were stabilized by the synergy of hydrophilic SiO_2 NPs and caprylamidopropyl betaine (CAPB) at 19.4 MPa and 50 °C. As CO_2 dissolves in the solution, it turns acidic. In these conditions, the surfactant becomes cationic and adsorbs onto the silica surfaces due to electrostatic attraction rendering them partially hydrophobic. Then, these couples anchored at the gas-liquid interfaces stabilize foams. As shown in Fig. 4, the synergy between zwitterionic surfactants below their isoelectric point (usually acid values) and SiO_2 NPs follows a trend similar to that of cationic surfactants, i.e., at moderate adsorbed surfactant concentrations, SiO_2 NPs turn hydrophobic enough to stabilize the interface. However, according to zeta potential measurements, unlike the cationic ones, zwitterionic surfactants do not adsorb in the form of bilayers on the silica surface. In a subsequent study, CO_2 foams containing SiO_2 NPs and the zwitterionic surfactant lauramidopropyl betaine (LAPB, in solution with other betaine surfactants at low concentration) were produced at 19.4 MPa and 50 °C too [120]. Beadpack results showed these foams as candidate systems to be used as displacement fluids in oil reservoirs, a statement that can be extended to foams studied in [119]. The potential use in EOR of CO_2 foams in which the hydrophilic silica nanoparticles-zwitterionic surfac-

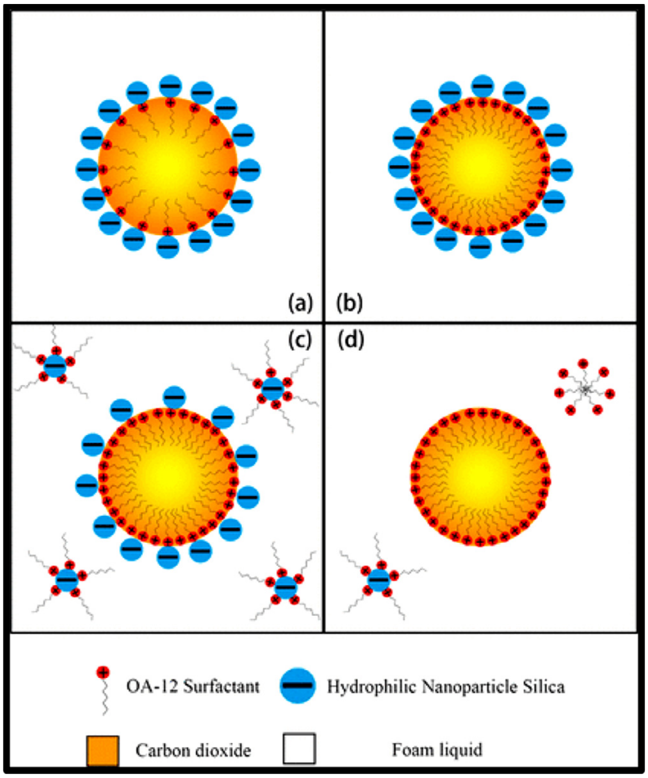


Fig. 4. Schematic representation of the mechanism of CO_2 foam stabilization by hydrophilic nanoparticles and a zwitterionic surfactant in an acidic medium: (a) inadequate surfactant concentration; (b) moderate surfactant concentration; (c) excess surfactant concentration; (d) surfactant and nanoparticles flocculation and precipitation. (Reproduced with permission [122] Copyright 2018, American Chemical Society).

tant synergy stabilizes interfaces was confirmed in a study performed by Li et al. [121] using hexadecyl hydroxypropyl sulfobetaine (HHSB) as a surfactant. They reported a marked foam stability at 70 °C and 8 MPa, and the positive role of salinity on bubbles stability. In addition, the rheological properties of the studied foam supported its application in oil recovery processes.

A comparative study between different surfactants and hydrophilic SiO_2 NPs on the stability of CO_2 foams was carried out using the Ross-Miles instrument as the foaming technique. The surfactants used in mixtures with SiO_2 NPs were CTAB (cationic surfactant), sodium dodecylbenzene sulfonate (SDBS, anionic surfactant), polyethylene glycol tert-octyl phenyl ether (Triton X-100 or TX-100, nonionic surfactant), and dodecyl dimethyl ammonium oxide (OA-12, zwitterionic surfactant) [122]. The foam produced with the zwitterionic surfactant presented higher stability than the others, even at elevated temperatures; however, attention should be paid to NPs flocculation observed at elevated surfactant concentration, as this may have adverse effects in EOR.

Interestingly, the synergy between SiO_2 NPs and short amphiphilic compounds (generally with less than 8 carbon atoms) such as alkylamines has been studied in foams stabilization following a similar mechanism as in the case of the cationic surfactants [123]. Alkylamines adsorb onto the silica surfaces due to electrostatic interactions, exposing their hydrophobic regions to the aqueous phase and modifying the nanoparticle wettability (hydrophobicity increases). Sandpack and plugging experiments carried out with nitrogen foams stabilized by bare SiO_2 NPs combined with hexylamine showed that the most stable foams, which occurred at intermediate hexylamine concentrations, were the most effective in these processes due to their breakage resistance in porous media. These observations were related to an increase in the dilational viscoelasticity and bubble roughness [124]. Also, foams generated with mixtures of propyl gallate and alumina-coated SiO_2 NPs demonstrated good results in Berea sandstone cores flow and oil displacement experiments [125]. These two last reports extend the synergistic SiO_2 NPs behavior to short compounds such as hexylamine and alkyl gallates, benefiting oil recovery operations and materials tailoring (as will be described in section 4.2).

4.1.2. Silica nanoparticles and anionic surfactants

Combinations of SiO_2 NPs and anionic surfactants stabilizing foams of different gases such as nitrogen, carbon dioxide, air, and others have been explored for EOR purposes. In a first study, Sun et al. [35] demonstrated that nitrogen foams' stability in a brine medium was enhanced, even at high temperatures, when moderately hydrophobic SiO_2 NPs are coupled with SDS. In addition, micromodel and sandpack flooding experiments indicated that oil recovery increased with nanoparticle concentration at a fixed SDS concentration of 0.5 wt%, reaching a steady value at a nanoparticle concentration of 1.5 wt%. Later, the same group reported that these foams showed much better stability, diversion, and oil displacement results compared to SDS foams [95,97].

Carbon dioxide foams stabilized by SiO_2 NPs and SDS have been recently employed in oil recovery experiments. The synergy between SDS and hydrophobic SiO_2 NPs stabilizing CO_2 foams offered better stability and performance in porous media at high temperatures than only SDS, particularly at an SDS/SiO_2 concentration ratio of 0.17 [126]. Risal et al. [29] reported pore plugging and flooding enhancement of CO_2 foams stabilized by mixtures of SDS and SiO_2 NPs with different wettability: hydrophilic (bare silica), weakly hydrophobic (60% Si-OH), and hydrophobic (40% Si-OH). Their results showed that foams stabilized with weakly hydrophobic nanoparticles were the most stable due to their intermediate contact angle, leading to a bridging stabilization mechanism. Furthermore, it was found that this foam recovered 75% of cumulative oil, the highest percentage compared to other foams, due to its structural resistance in porous media. The mechanical strength of SDS-SiO_2 NPs based foams has been explained as a consequence of nanoparticle interfacial attachment and aggregation at the liquid films between two bubbles (lamellae), which present a wider thickness compared to SDS stabilized foams [127]. Also, CO_2 foams were the basis to show that SDS-SiO_2 NPs coupling reduces SDS adsorption onto kaolinite surfaces, which suggests this synergy can be used to diminish surfactant adsorption on clay minerals, upgrading the foam behavior in porous media [128].

A comparative study between air and carbon dioxide foams, both stabilized by mixtures of SDS and hydrophilic, hydrophobic SiO_2 NPs (50% Si-OH) or aluminum oxide nanoparticles (Al_2O_3) was performed by Yekeen et al. [129]. Air foams were most stable than the CO_2 ones due to the high solubility of CO_2 in water; on the other hand, hydrophobic SiO_2 NPs (in synergy with SDS) were more favorable as foam stabilizers than hydrophilic and aluminum oxide nanoparticles since the hydrophobic ones attach stronger at the interface. Hele-Shaw cell observations allowed predicting that air foams stabilized by SDS and hydrophobic SiO_2 NPs may result in a promising system for propagation in porous media. The same group also evaluated the effect of four oils (crude oil, paraffin oil, decane, and hexadecane) on the stability of foams stabilized by SDS and the two types of SiO_2 NPs just mentioned [130]. The experiments revealed that foams are more susceptible to downfall in the presence of oils with low viscosity and density, as their spreading coefficients (tendency to spread) on the interfaces are large, which causes film thinning and further foam breakdown.

Albeit SDS has been the most employed anionic surfactant coupled to SiO_2 NPs for foams stabilization, other anionic surfactants, as alpha-olefin sulphonate (AOS), have also been evaluated in different researches. Studies on carbon dioxide foams stabilized by AOS and hydrophobic SiO_2 NPs pointed out that a bigger nanoparticle size offers better foam stability when a lower nanoparticle concentration is present. In contrast, the smaller nanoparticles provide better results at high concentrations [131]. Recently, a systematic rheological study of N_2 and

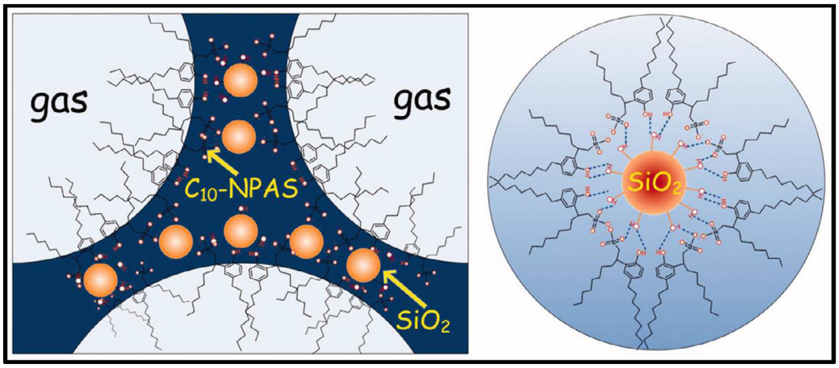


Fig. 5. Representation of the activation mechanism of nanosilica by the anionic surfactant C_{10}–NPAS. (Reproduced with permission [86] Copyright 2019, Taylor & Francis Group, LLC).

CO_2 foams stabilized by hydrophilic SiO_2 NPs, and AOS was carried out by Du et al. [132], which provided useful rheological information for oil recovery and carbon storage processes. From this research, it was concluded that N_2 foams present higher viscosity and better rheological properties than CO_2 foams and that, although the presence of sodium chloride decreases the viscosity of CO_2 foams, oil does not seem to have a viscosity effect on this type of foam.

Foams stabilized with the anionic surfactant sodium dodecyl benzenesulfonate (SDBS), and SiO_2 NPs have also been reported, interestingly, in hydraulic fracturing applications. Lv et al. [133] investigated the surface and bulk rheology, filtration, and proppant settling velocity of nitrogen foams containing SDBS and partially hydrophobic SiO_2 NPs, concluding that stability and thermal adaptability of SDBS foam increased when nanoparticles were present. It was also shown that the proppant-carrying ability of SiO_2 NPs-SDBS foam considerably increased compared to SDBS foam and that its core damage was low. Proppant-carrying capacity is relevant in hydraulic fracturing since it guarantees the fracturing fluid can retain open the wellbore fractures [134]. In a later report, a mixture of SDBS, SDS, and erucyl amidopropyl betaine (zwitterionic surfactant EAPB) to which SiO_2 NPs were added, evidenced the remarked role of nanoparticles in enhancing air foam stability and fracturing conductivity, achieving a better proppant suspension [135]. Other goals of this investigation were to provide a hydraulic fracturing model, and general remarks on the use of surfactant-SiO_2 NPs stabilized foams for hydraulic fracturing operations.

Although the vast majority of the anionic surfactants used in combination with SiO_2 NPs to stabilize foams for EOR applications rely on the studies so far mentioned, other interesting studies involving other anionic surfactants are found in the literature. In a recent report, partially hydrophobic SiO_2 NPs combined with sodium lauryl sulfate (SLS) were used to generate and stabilize N_2 foams in a porous medium using a microfluidic chip [136]. Interestingly, it was concluded that the generation of foams with and without nanoparticles share the same classical constitutive equation, shedding light on the birth and death throughout porous media of foams stabilized by SiO_2 NPs and surfactants. Lately, the use of N_2 foams stabilized with partially hydrophobic SiO_2 NPs and the FRC-1 anionic surfactant in EOR applications under high temperature was experimentally and numerically evaluated [34]. FRC-1 is a clean fracturing fluid composed of: 2.5% viscoelastic surfactant, 0.1% special stabilizing agent, and the corresponding balance of 4% saline water [137]. Micromodel experiments showed that foams containing SiO_2 NPs-surfactant were more stable against coalescence and coarsening than foams elaborated only with a surfactant, whereas the sandpack flooding tests evidenced an enhanced oil recovery too. The simulation study confirmed these last results. On the other hand, Long et al. [86] explored air foams stabilized by hydrophilic SiO_2 NPs and the nonylphenol-substituted decylsulfonate surfactant C_{10}–NPAS, reporting the in-situ activation of SiO_2 NPs by C_{10}–NPAS through hydrogen-bonds interactions with the phenolic hydroxyl groups and the subsequent particle location in the liquid films, providing resistance to bubble coalescence, as shown in Fig. 5. They also proposed a method for solid foam characterization based on the use of poly(vinyl alcohol) (PVA) as a supporter. Since the obtained solid soft materials provide insights into the foam structure, this last technique can be useful to characterize diverse nanoparticle-stabilized aqueous foams.

According to a recent work [138], binary surfactant systems of an internal olefin sulfonate series (IOS) and sodium polyethylene glycol monohexadecyl ether sulfate ($C_{32}H_{66}Na_2O_5S$), can act together with hydrophobic SiO_2 NPs to enhance the stability of air foams with either deionized water (DI) or bine as the continuous phase. This research also analyzed the effect on foam stability of the length of the surfactant's tail and the presence of alkane oils with different chain lengths, offering valuable information for foam flooding processes where hydrocarbons and brines are involved. Fatty alcohol polyoxyethylene ether sodium sulfates (AES) constitute an anionic-nonionic surfactant class whose synergy with alumina-coated SiO_2 NPs has also been successfully used to stabilize methane (natural gas) foams in the presence of oil and salt, creating an optimal flow through porous media in contact with oil [84]. Two stabilization mechanisms were indicated: an increase of the interfacial dilatational elasticity and the presence of flocs in the foam structure. Moreover, the addition of salt aided the foam stability at high temperatures, constituting an advantage since the presence of salt mimics the conditions in reservoirs [84,139]. Even more, AES demonstrated a better synergistic effect with alumina-coated SiO_2 NPs than SDS since SDS interacts with SiO_2 NPs through electrostatic attraction, whereas AES do it through both electrostatic attraction and hydrogen bonds [139]. Other anionic surfactants in combination with SiO_2 NPs coated with polyethylene glycol (PEG) have been used in the stabilization of nitrogen [87,140] and air [141] foams for EOR operations.

Although different surfactants can be useful in EOR, the selection will be made based on the minimum adsorption on oil reservoirs since surfactant loss implies economic issues. In this manner, cationic surfactants could not be appropriate for sandstone reservoirs, whereas anionic surfactants may be avoided in processes involving carbonate reservoirs [142].

4.1.3. *Silica nanoparticles and nonionic surfactants*

In a similar trend to foams stabilized by SiO_2 NPs and cationic/anionic surfactants, gas dispersions containing SiO_2 NPs and nonionic surfactants have attracted great interest in EOR and related operations. Dynamic tests experiments of nitrogen foams containing hydrophilic SiO_2 NPs and alcohol ethoxylate nonionic surfactants indicated that these foams were resistant in porous media, a characteristic desired in gas mobility control. Foam stability was explained in terms of flocs formation, which diminished coalescence and drainage rate [105]. In recent years, Li et al. [99] studied the synergistic interactions between lauryl alcohol polyoxyethylene ether ($C_{12}E_{23}$) and different hydrophilicity degree SiO_2 NPs on stabilization of CO_2 foams. They found that the synergistic effect was more pronounced for nanoparticles with higher hydrophilicity and that foams stabilized by mixtures of these nanoparticles and $C_{12}E_{23}$ presented the highest sweep efficiency, enhancing oil recovery in porous media. The authors also explained the

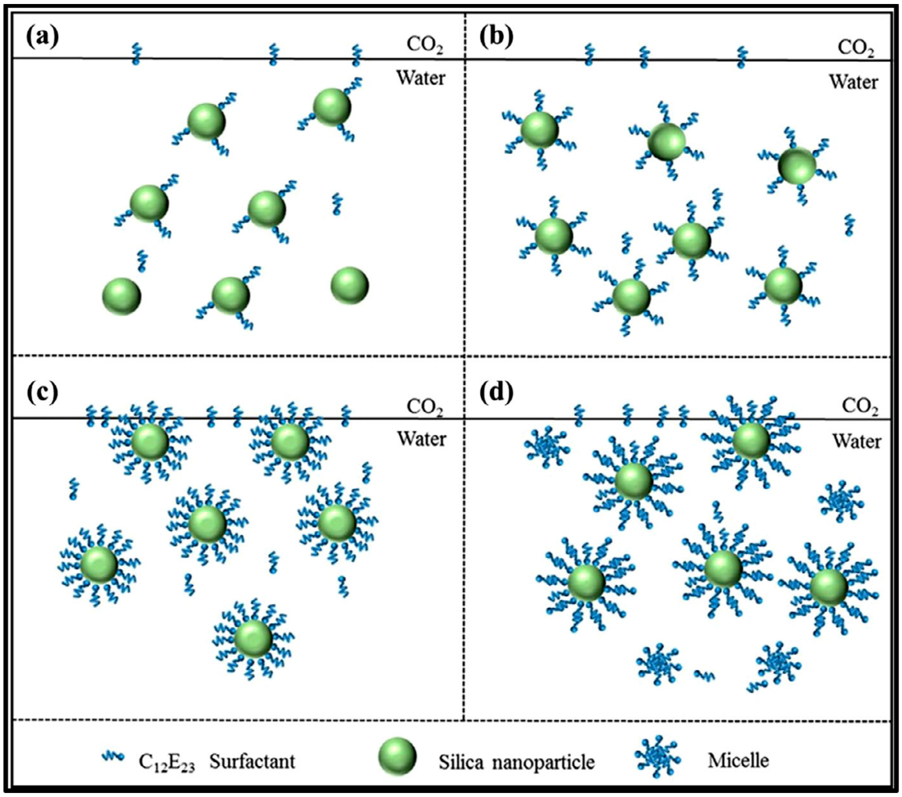


Fig. 6. Sketch of nanoparticles' adsorption at the CO_2-water interface with increasing $C_{12}E_{23}$ concentration from (a) to (d). (Reproduced with permission [99] Copyright 2019, American Chemical Society).

different surfactant adsorption stages developed when the surfactant concentration is varied at a fixed nanoparticle amount. At a low surfactant concentration, hydrophilic nanoparticles are not able to stabilize the CO_2 foams (Fig. 6a); however, when the surfactant concentration increases, a loose $C_{12}E_{23}$ monolayer is formed on the nanoparticle surface, which augments their foam stabilization capacity (Fig. 6b). By increasing surfactant concentration, a dense surfactant monolayer is formed on the nanoparticle surface, the optimal nanoparticle hydrophobicity is reached and the optimal surfactant-nanoparticle synergy for CO_2 foams stabilization is exhibited (Fig. 6c). Lastly, at higher surfactant concentrations, surfactant adsorbs as a double layer onto silica surfaces, nanoparticles turn hydrophilic again, the foam stability decreases, and micelles are also formed (Fig. 6d).

4.2. Materials engineering

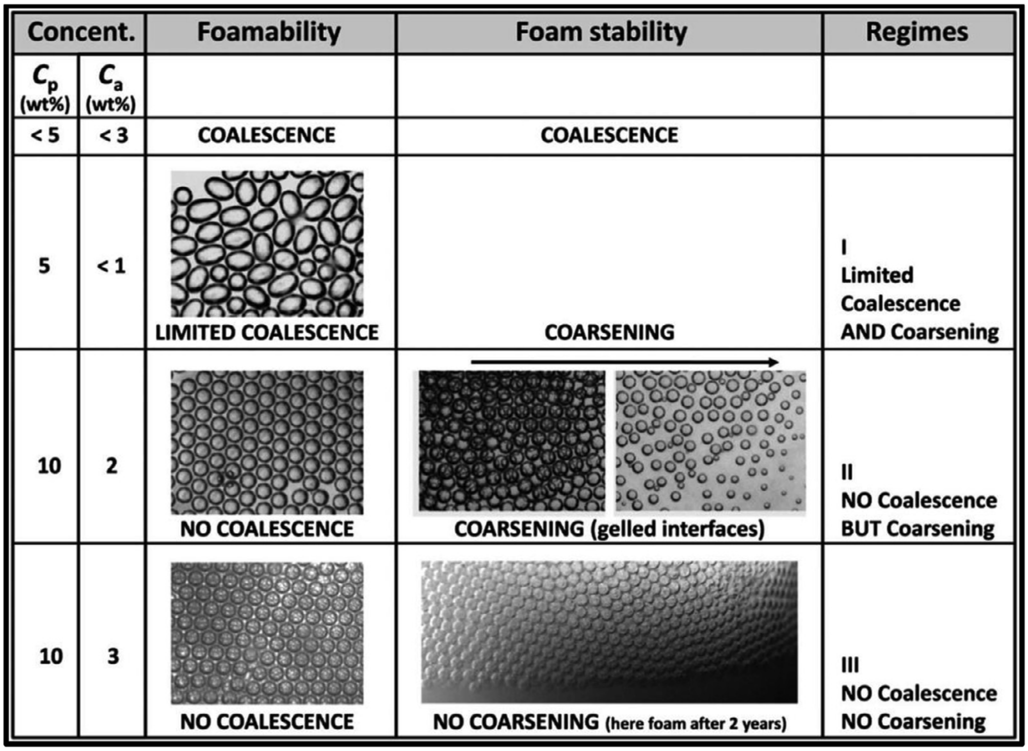
Some reports on foams stabilized by the combined effect of SiO_2 NPs and surfactants have notoriously influenced materials research. On the one hand, different methodologies for producing responsive foams without requiring complex formulations have been developed. This is relevant in applications where foams are temporarily required, for example in certain cosmetic products, as well as in foam flooding and floating. On the other hand, studies on foams stabilized by mixtures of surfactants and nanoparticles have opened a course for elaborating porous materials that may be used as catalysts, separation media, and even biomedical scaffolds [143].

4.2.1. Responsive foams and innovative formulations

One way to obtain responsive/switchable foams is the electrostatic play between hydrophilic SiO_2 NPs, a cationic surfactant (CTAB or DTAB), and an anionic surfactant (SDS). These foams can be stabilized by a precise amount of cationic surfactant and destabilized by the addition of an equal quantity (moles) of anionic surfactant, and so on for many cycles [144]. Zwitterionic surfactants offer the possibility to elaborate responsive foams, too, as was recently explored using dodecyl dimethyl carboxyl betaine ($C_{12}B$) and hydrophilic SiO_2 NP, varying the pH [145]. The surfactant became cationic at pH < 4, adsorbed on the silica's surface, and stabilized air-water interfaces. If pH went higher than 10, the surfactant turned zwitterionic again, the adsorption onto SiO_2 NPs was reduced since electrostatic interactions diminish, and then foams collapsed. Currently, pH-controlled nitrogen foams have been elaborated for potential use in EOR. These foams, stabilized by mixtures of fatty alcohol ethoxylated carboxymethylated surfactants and partially hydrophobic SiO_2 NPs, exhibited the highest foam stability and oil displacement efficiency at pH = 9, a consequence of the deprotonation process [146]. Despite this last report does not present the studied foams as responsive systems, it offers a new and accessible chemical recipe to control the foam stability according to particular needs.

In a striking study, it was observed that the addition of SDS caused the transition from liquid marbles to aqueous foams as hydrophobic SiO_2 NPs became more and more hydrophilic [147]. In other words, a transition from macroscopic aqueous drops to bubbles (both stabilized by SiO_2 NPs and surfactants) was achieved. The transition reported offers a practical method to obtain liquid foams and liquid marbles from the same original system, which is advantageous because of the feasible applications of liquid marbles in cosmetics formulation and micro-reactors design, among others [148,149].

Two novel foams for material formulations have been just communicated. One study focuses on foams elaborated with hydrophilic SiO_2 NPs, CTAB, and FS-50 (a short-chain fluorocarbon surfactant) as a starting point for using surfactant-SiO_2 NPs foams in firefighting applications [150]. The other work presented, through small-angle neutron scattering (SANS) experiments and molecular dynamics (MD) simulations, different scenarios of the adsorption of a fatty acid (decanoic acid) onto the surface of propylamine-functionalized SiO_2 NPs: patchy aggregates or monolayers. Authors discussed the link between the fatty acid adsorption form on SiO_2 NPs and the stability of foams elaborated with these mixtures, and suggest that the information obtained may be of interest in the design of cosmetics and food foams [38].



Concent.		Foamability	Foam stability	Regimes
C_p (wt%)	C_a (wt%)			
< 5	< 3	COALESCENCE	COALESCENCE	
5	< 1	LIMITED COALESCENCE	COARSENING	I Limited Coalescence AND Coarsening
10	2	NO COALESCENCE	COARSENING (gelled interfaces)	II NO Coalescence BUT Coarsening
10	3	NO COALESCENCE	NO COARSENING (here foam after 2 years)	III NO Coalescence NO Coarsening

Fig. 7. Monodisperse foams were obtained at various amine concentrations (c_a) and two particle concentrations (c_p), 5 and 10 wt%. For $c_p < 5$ wt% foams could not be created in the microfluidic device in the defined range of amine concentrations, evolving by coalescence. For $c_a = 1$ wt%, at $c_p = 5$ wt% and $c_p = 10$ wt%, limited coalescence and almost no coalescence is observed, respectively. At $c_p = 10$ wt%, coarsening is still present. At higher c_a, coarsening is also stopped and bulk gelation is observed. All bubble sizes are around 500 μm. (Reproduced with permission [152] Copyright 2012, The Royal Society of Chemistry).

4.2.2. *Elaboration of macroporous materials*

Gonzenbach et al. [123,151] visualized a method to tailor porous materials starting from wet highly-stable foams stabilized by different mixtures of particles and amphiphiles, including the combination of hydrophilic SiO_2 NPs and hexylamine. The authors found out that foam air content and bubble size could be controlled by varying particle size, the type of amphiphile, and the concentration of both elements. However, a clear picture of foam stabilization by the synergistic effect of SiO_2 NPs and an alkylamine (n-amylamine) was offered years later by Arriaga et al. [152] in a study where monodisperse foams were produced with a microfluidic technique. In this work, different stability schemes depending on the nanoparticle and amylamine concentration were observed. A limited coalescence regime followed by coarsening is observed for amylamine concentrations ≈ 1 wt% and nanoparticle concentration of 5 wt%. By increasing both nanoparticle and amylamine concentrations, coalescence was suppressed, and foams evolved just by coarsening. By adding more amylamine, coalescence and coarsening were stopped entirely, likely due to bulk gelation. The three stages discussed are depicted in Fig. 7. It is known that as alkylamines adsorb on hydrophilic SiO_2 NP, the surface coverage increases up to a point where nanoparticle aggregation occurs due to hydrophobic interaction between alkylamines chains. The formed aggregates trigger the system gel formation, which heightens foam stability [153].

5. Literature review of SiO_2 nanoparticles-surfactants emulsions in different research fields

5.1. *Enhanced oil recovery (EOR)*

Both emulsions' injection into petroleum reservoirs and the in situ emulsion formation have triggered attention in EOR, especially when working with heavy oils. By diverting the flow to unswept zones and entraining oil into the continuous phase, emulsion flooding provides remarkable efficiency sweeps [154–157]. Nonetheless, a requirement for emulsions to be used in EOR is a high lifetime, where emulsions stabilized by SiO_2 NPs-surfactants mixtures have found a prominent position in petroleum recovery.

After performing core flooding experiments (using crude oil) and microscopic observations, Pei et al. [158] concluded that biodiesel-in-brine water emulsions with interfaces stabilized by hydrophilic SiO_2 NPs-CTAB, induced higher tertiary oil recoveries (reaching increments of over 40%) and sweep efficiency compared to only surfactant-stabilized emulsions. Emulsions formulated with mixtures of SiO_2 NPs and CTAB could present higher stability and viscosity than SDS-SiO_2 NPs stabilized emulsions due to electrostatic interactions between CTAB and silica surfaces [89]. Nevertheless, It is necessary to analyze interfacial tension reduction, rock wetting properties, and emulsion stability altogether to select a system for enhanced oil displacement and porous media processes [159].

At present, emulsions elaborated with anionic surfactants and SiO_2 NPs are also of interest in petroleum engineering. Lin et al. [160] performed an investigation on diesel oil-in-water emulsions stabilized by mixtures of SiO_2 NPs and traces of the anionic surfactant SDBS. The destabilization of diesel oil-in-water emulsions happened when adding small amounts of either CTAB or $CaCl_2$ (calcium chloride), which implemented an easy demulsification method with possible oil transportation application. Another recent study reported that emulsions containing SiO_2 NPs and SDS showed a remarkable viscosity increase compared to those without nanoparticles, although for SiO_2 NPs-CTAB emulsions this increase was more marked [161]. In any case, the viscosity increase in both types of emulsions could be advantageous for possible uses in permeability profile modification. Interestingly, petroleum sulfonate (PS, an anionic surfactant mixture of different polarity fractions [162]) has recently proved to be a good emulsifier combined with silane-modified SiO_2 NPs for crude oil/water dispersions [98]. The data obtained in this last report are significant since PS has a strong presence in oil recovery operations [163].

5.2. Materials engineering

In the last decade and analogous to foams, SiO_2 NPs-surfactants stabilized emulsions have positively impacted materials research. While in many cases a long-stable emulsion is desired, in some applications, a controlled emulsion formation and collapse (or inversion) is needed, as in oil transport and active ingredients release. Then, the formulation of responsive emulsions has emerged, not only for surfactant emulsions but for those including SiO_2 NPs. Elaboration of porous materials is another research line where emulsions stabilized by surfactants and SiO_2 NPs have gained interest, as these materials involve potential applications in catalysis, tissue engineering, and thermal processes [164]. Recently, the manufacturing applications of emulsions stabilized by SiO_2 NPs and surfactants opened a new path (3D-printing of Newtonian fluids) since the formation of tubules and cylindrical emulsion droplets has been reached [165].

5.2.1. Responsive emulsions

A double phase inversion in emulsions was reported for water-*n*-dodecane dispersions stabilized by mixtures of hydrophilic SiO_2 NPs and the di-chain surfactant didecyldimethylammonium bromide (di-C_{10}DMAB) [166]. Increasing the amount of di-C_{10}DMAB at a fixed nanoparticle concentration produces a double inversion. First, the change from O/W to W/O emulsion comes up as a result of a surfactant monolayer adsorbed on silica surfaces that turns nanoparticles hydrophobic. When more surfactant is added, a transition from W/O to O/W emulsion occurs due to a surfactant bilayer formation on the nanoparticle's surface that turns nanoparticles hydrophilic again. Two additional double-chain surfactants with different hydrocarbon chain lengths (8 and 12 carbons) were later considered [167]. The double emulsion inversion was observed for these two surfactants in a similar trend to di-C_{10}DMAB cases, although in the case of di-C_{12}DMAB double emulsions were formed at surfactant concentrations in the vicinity of inversion limits. It was also demonstrated that double inversion could occur by increasing the nanoparticle amount at a fixed surfactant concentration. A novel method to induce an O/W to W/O inversion and vice versa in emulsions stabilized by hydrophilic SiO_2 NPs and N-(2-((2-aminoethyl)amino)ethyl)octadecenamide (C_{18}PDA surfactant) was developed by Liu et al. [168]. Inversions were triggered by modulating the surfactant-nanoparticles interactions in the presence of the sodium carbonate salt (Na_2CO_3), up to the point of high salt concentration where demulsification occurs. The system's peculiar rheological properties at the transition point, their efficiency in the filter-cake cleanup, and the no need for extreme pH conditions convert these emulsions into a green possibility in drilling procedures.

Curiously, the synergistic interaction of hydrophilic SiO_2 NPs with single-chain cationic surfactants as CTAB, DTAB, or with the gemini surfactant trimethylene-di(tetradecacyloxyethyldimethylammoniumbromide) (II-14–3) stabilizes O/W emulsions (toluene-in-water) but does not promote the O/W to W/O emulsion inversion [169]. On the contrary, a double-chain cationic surfactant does induce a double emulsion inversion since the density of hydrocarbon chains adsorbed on the nanoparticles is enhanced, increasing the nanoparticles' hydrophobicity up to a value where phase inversion is possible. Also, it was recently reported that mixtures of hydrophilic SiO_2 NPs with either multiple quaternary ammonium salts (MQAS-12) or bis-quaternary ammonium salts (BQAS-12) do not induce emulsion inversion from O/W to W/O [170].

Emulsions stabilized with SiO_2 NPs-cationic surfactants can become unstable by adding a certain amount of an anionic surfactant (Fig. 8a and 8b), as was observed for dodecane-in-water emulsions (as well as for toluene-in-water and tricaprylin-in-water emulsions) containing hydrophilic SiO_2 NPs in combination with CTAB or DTAB, in which an equimolar amount of sodium alkylsulfates (C_6–C_{12}) was added [171]. The explanation for this behavior was the ion-pairing formation between the cationic and anionic surfactants, which causes the desorption of cationic surfactants from the silica surface. The restabilization of the emulsions was possible by adding the corresponding amount of cationic surfactant again and so on. Whereas alkyl sulfates with chain lengths of 10 and 12 carbons were effective demulsifiers for samples with CTAB or DTAB, shorter alkyl sulfates (6 and 8 carbons) did not have a demulsifier effect in DTAB samples. They had only a slight effect in CTAB emulsions, suggesting that a minimum number of total carbons are required to induce demulsification (Fig. 8c and 8d).

Another approach for emulsions control was proposed by Jiang et al. [172] in a study where the surfactant *N*'-dodecyl-*N,N*-dimethylacetamidinium bicarbonate, in synergistic effect with hydrophilic SiO_2 NPs, stabilized *n*-octane-in-water emulsions, which were destabilized and restabilized by bubbling N_2 and CO_2, respectively, inducing the surfactant cationic form (active) and the neutral one (inactive). However, the temperatures needed to trigger the emulsion stability changes are high for N_2 and low for CO_2, constituting a limitation in the process. In some instances, varying the pH values allows having a stable or unstable emulsion. Switchable water-in-diesel oil emulsions were obtained based on the pH response of SiO_2 NPs and C_{18}PDA surfactant, remaining stable at pH 2–12 but demulsified at extreme pH values [173]. At extreme acidic conditions, the amine protonates, and a strong electrical repulsion between amine groups and SiO_2 NPs prevents nanoparticles' adsorption at the oil-water interface. In contrast, in an extremely basic medium, the electrical repulsion between nanoparticles does not allow silica flocculation, and nanoparticles are dispersed in the aqueous phase. pH-responsive emulsions can be also prepared based on the synergistic effect of hydrophilic SiO_2 NPs-dodecyldimethylcarboxylbetaine (C_{12}B, a zwitterionic surfactant) [174]. Droplets in toluene-in-water and *n*-decane-in-water emulsions were stable to coalescence at $pH \leq 5$ and suffered total phase separation at $pH > 8.5$; this means emulsions could be switched from stable in an acidic medium (surfactant in the cationic form) to unstable in a basic one.

Interestingly, temperature-responsive toluene-in-water and dodecane-in-water emulsions can be produced by mixing hydrophilic SiO_2 NPs with small amounts of an alkyl polyoxyethylene monododecyl ether nonionic surfactant ($C_{12}E_2$, $C_{12}E_3$, $C_{12}E_4$, $C_{12}E_{5,}$ and $C_{12}E_{10}$) [175]. At room temperature, emulsions were stable for months, but submitted to high temperatures and stirring, they presented phase separation in a couple of hours or tens of minutes, depending on the temperature imposed, surfactant concentration, and head group length. Then, the emulsion was restored when cooled at room temperature and homogenized. It was demonstrated that this destabilization-stabilization process could be cyclically continued. As temperature increases, hydrogen bond interactions between the nonionic surfactant and SiO_2 NPs lose strength, and so does emulsion stability. With this method, a practical and more ecological route to obtain responsive emulsions is proposed for cases where the required energy for heating/cooling can be supplied without further problems.

An antagonistic effect between SiO_2 NPs and nonionic surfactants has been observed in some emulsified systems. Katepally et al. [176] studied how SiO_2 NPs with different hydrophobicity degrees influenced hexadecane-in-water emulsions stabilized by Triton X-100. When hydrophilic nanoparticles were added, droplet ripening and flocculation took place, appearing nanoparticle aggregation at high concentrations, but no phase separation was evidenced. However, emulsions suffered a total phase separation when partially hydrophobic SiO_2 NPs were added (Fig. 9a and 9b). Although hydrophilic nanoparticles interact with silica surfaces through hydrogen bonding and induce surfactant depletion at the oil-water interface, this depletion is not strong enough to cause phase separation. Partially hydrophobic SiO_2 NPs, instead, interact with the nonionic surfactant through hydrophobic interactions, highly promoting surfactant depletion and, consequently, emulsion destabilization oc-

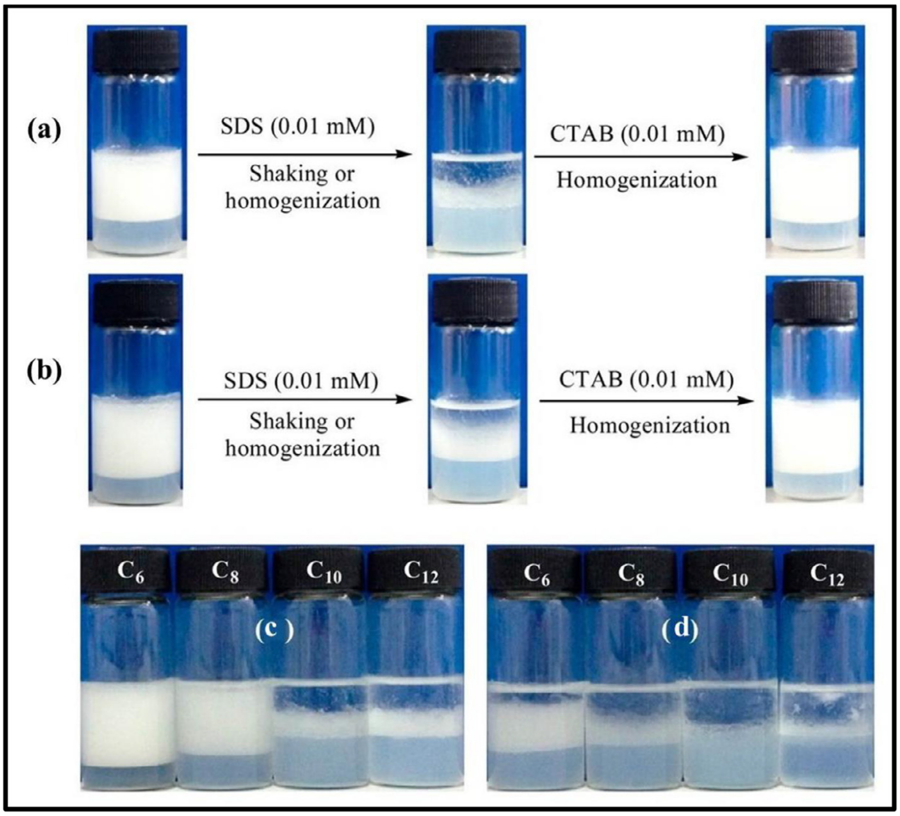


Fig. 8. Switching between stable and unstable (a) toluene-in-water emulsion and (b) tricaprylin-in-water emulsion, both 1:1 emulsions, containing 0.5 wt% silica nanoparticles in combination with 0.01 mM CTAB with the successive addition of 0.01 mM SDS, and subsequently 0.01 mM CTAB. Pictures were taken 24 h (stable) and 30 min (unstable) after surfactant addition, respectively. Demulsification of dodecane-in-water (1:1) emulsions stabilized by (c) 0.5 wt% silica + 0.1 mM DTAB, or (d) by 0.5 wt% silica + 0.01 mM CTAB, by adding an equimolar amount of sodium alkylsulfate of different chain lengths (indicated) followed by handshaking. Pictures were taken 2 h after shaking. (Adapted with permission [171] Copyright 2015, American Chemical Society).

curs, as portrayed in Fig. 9c. The same effects were later witnessed after the addition of SiO_2 NPs of different hydrophobicities in cyclohexane-in-oil emulsions stabilized by sorbitan monooleate (SPAN 80) [177]. Whereas the addition of hydrophilic and hydrophobic nanoparticles led to an inefficient and no emulsion destabilization, respectively, partially hydrophobic nanoparticles did demulsify the surfactant-stabilized emulsions. This work explained that hydrophobic nanoparticles did not act as demulsifiers due to the weak hydrophobic interactions with the nonionic surfactant. Cases in which the release of nanoparticles occurred have been also addressed. It was demonstrated that the interfacial displacement of partially hydrophobic SiO_2 NPs from oil-water interfaces is promoted by adding an anionic surfactant (SDS) above the critical micelle concentration and mixing [178,179]. These results may be relevant for rapid liberation of a cosmetic/drug from droplets.

There is no doubt that low-cost systems are desired in all the applications where emulsions are involved; consequently, studies in which emulsions require low quantities of surfactant to be stabilized are relevant. Small amounts of the zwitterionic surfactant CAPB, with a high hydrophilic-lipophilic balance (HLB) value, mixed with hydrophilic SiO_2 NPs, have been effectively used to stabilize dodecane-in-water emulsions [180]. Because of the high surfactant CMC and its weak adsorption on the nanoparticles' surface, a large surfactant amount can adsorb at the oil-water interface, lowering the interfacial tension and leading to the generation of small stable droplets. In the last couple of years, reports on emulsions stabilized by very low concentrations of both hydrophilic SiO_2 NPs and SDS [181] or SDBS [182] have been presented. Since surfactant and SiO_2 NPs are like-charged, droplets are scarcely nanoparticle-surfactant coated, and nanoparticles are dispersed in the continuous phase. Whereas repulsion between droplets diminishes coalescence events, the dispersed nanoparticles decrease the creaming rate, and droplet flocculation and coalescence. However, in all emulsion formulations, the effect of mixing conditions [88] and the oil phase's polar character [22] should be taken into account, as these factors influence emulsion stability.

5.2.2. *Elaboration of macroporous materials*

A method to tailor hierarchical porous materials from toluene droplets stabilized by CTAB-SiO_2 NPs was described by Studart et al. [36]. This technique mainly relied on two processes: production of monodisperse micrometric droplets and drying. The obtention of a closed or interconnected macroporosity depended on the interfacial stabilizing agent (nanoparticles or surfactant molecules). As in foams, short compounds as hexylamine can act synergistically with SiO_2 NPs for emulsion stabilization [183]. It was observed that this synergy significantly improved the stability of octane-in-water emulsions, hindering droplet coalescence and Ostwald ripening. In virtue of their high stability and the feasibility of tuning their microstructure, these emulsions can be used as a starting point in the fabrication of macroporous ceramics following a process that includes emulsification, drying, and sintering [37].

Water-in-styrene high internal phase emulsions (HIPEs) stabilized by hydrophobic SiO_2 NPs and sorbitantrioleate (Span 85) have been used as templates for polymerization and elaboration of hierarchically porous materials tailored by modifying the nanoparticle and surfactant concentrations [106]. Hence, surfactant-nanoparticle stabilized HIPEs constitute a path for developing porous materials with applications in catalysis and biomedical engineering scaffolds, among others. It is possible that, in future years, SiO_2 NPs-surfactants stabilized emulsions will expand their applications in catalysis without the need of elaborating a macroporous material, i.e., in their liquid form, as the case of particle-stabilized emulsions [184].

5.3. *Food and farmaceutical engineering*

Elaboration of food products has motivated the exploration of surfactant-nanoparticle stabilized emulsions prepared with "food-grade" surfactants and oils. Pichot et al. [39] analyzed the stability of vegetable oil-in-water emulsions containing hydrophilic SiO_2 NPs and monooleate-1-glycerin (monoolein), a nonionic surfactant of natural ori-

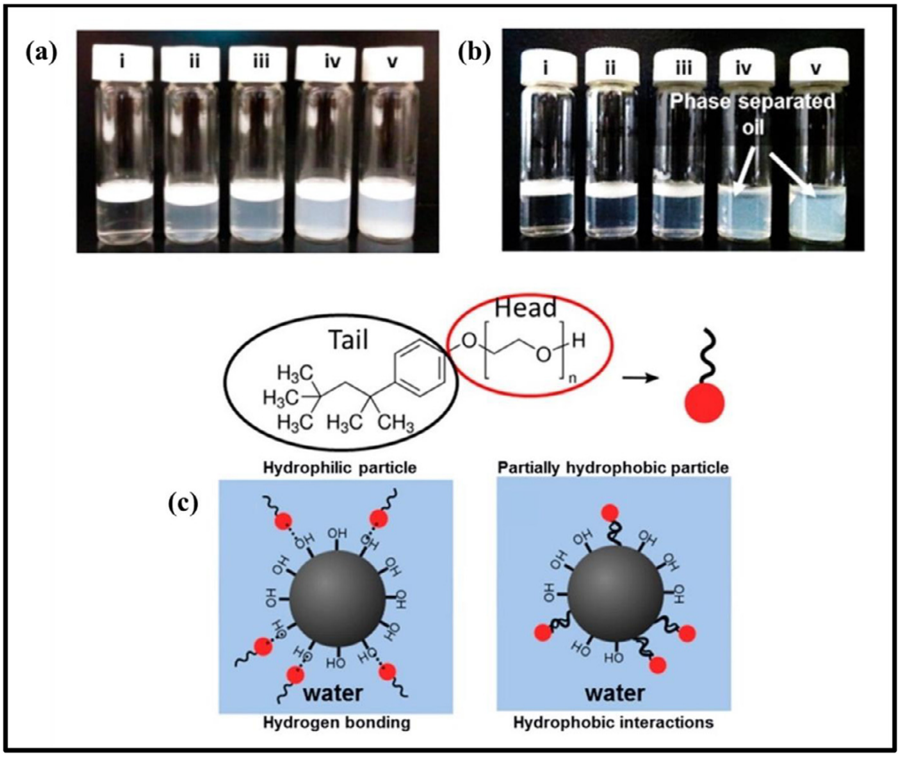


Fig. 9. Pictures of Triton-X-100-stabilized hexadecane-in-water emulsions with increasing concentrations (in wt%) of added hydrophilic (A200) and partially hydrophobic fumed silica particles (R816) in the aqueous phase. (a) A200: (i) 0, (ii) 0.05, (iii) 0.1, (iv) 0.5, and (v) 1, creaming (migration to the top) of the emulsion droplets is observed, but no visible phase separation of oil and water. (b) R816: (i) 0, (ii) 0.05, (iii) 0.1, (iv) 0.5, and (v) 1, creaming of the emulsion droplets is observed; visible phase separation of oil and water is visible above 0.5 wt%. (c) Schematic representation of adsorption behavior of Triton-X-100 nonionic surfactant molecules on particle surfaces of different hydrophilicities. Left: hydrogen bonding between the ethoxylated head groups and OH groups on the hydrophilic fumed silica particle surface. Right: hydrophobic interactions between the alkyl groups of the surfactant tails and the silanized fumed silica particle surface. (Adapted with permission [176] Copyright 2016, American Chemical Society).

gin. The authors proposed that the stability of the prepared emulsions is supported in a two-faced mechanism. Monoolein acts delaying droplet coalescence and reducing interfacial tension aiding nanoparticles to attach at the oil-water interfaces and therefore stabilize the emulsion. Both nanoparticle and monoolein concentrations were the main parameters on which the stabilization mechanism relies. In another study performed by the same authors [185], the synergistic interaction between hydrophilic SiO_2 NPs and surfactants with different HLB values on stabilizing vegetable oil-water emulsions was examined. The surfactants chosen were lecithin (HLB $\sim$ 4), polyoxyethylene sorbitan monostearate (Tween 60, HLB = 14.9), and sodium caseinate (NaCaS, HLB $\sim$ 14). Due to surfactant HLB values, emulsions containing Tween 60 or NaCaS were O/W type, whereas those with lecithin were W/O type, and although the three kinds of emulsions prepared showed stability against coalescence, a different effect resulted as surfactant concentration was varied. In O/W emulsions, SiO_2 NPs were shifted to the continuous phase when surfactant concentration augmented, up to a point where nanoparticles-surfactant emulsions behave as surfactant-stabilized since surfactant strongly competes with nanoparticles for a “position” at the interface (Fig. 10). W/O emulsions, in turn, did not suffer interfacial nanoparticle removal and were stable at any surfactant concentration.

SPAN 80 is a nonionic surfactant frequently used as a food additive. Some efforts to prepare emulsions with SiO_2 NPs and this surfactant have been carried out; in this manner, the techniques and results could be somehow extrapolated to food engineering. Drelich et al. [186] verified the excellent stability of water-in-paraffin oil emulsions stabilized by the synergy of hydrophobic SiO_2 NPs and SPAN 80, compared to that observed for just SPAN 80-stabilized emulsions. This enhanced emulsion stability was later attributed to a structural network formed by droplets bridged through nanoparticles [187].

In another work [188], SPAN 80 was chosen to study its synergistic effect with SiO_2 NPs presenting different hydrophobicity degrees in highly concentrated emulsions (HCE) of overcooled solutions of inorganic salts in a paraffin compound. The authors observed that all surfactant/nanoparticle ratios exhibit a transitional point below which the nanoparticle concentration controlled the emulsion stability, whereas surfactants controlled above this point. Emulsions showed their highest stability when prepared at this transitional point and it was proposed that the highest stability was reached when surfactant reverse micelles induced maximum particle flocculation. A recent investigation demonstrated that the addition of SPAN 80 to water-in-1-bromohexadecane dispersions stabilized by silica nanoparticles had a notorious influence on the emulsions’ rheological properties, depending on the wettability of the nanoparticles [189]. Whereas the viscosity of emulsions containing hydrophobic nanoparticles increased after the addition of SPAN 80, the viscosity of emulsions with partially hydrophobic nanoparticles decreased. These findings offered a practical method to modify the flowing properties of emulsions.

On the other hand, it is well known that emulsions constitute a valuable system in pharmaceutical engineering, and those elaborated with silica nanoparticles and surfactants are not the exception. Eskandar et al. [190] studied dispersions of Miglyol 812 (caprylic/capric triglyceride) in water stabilized with the combination of either lecithin or oleylamine and hydrophilic SiO_2 NPs. Emulsions containing Miglyol 812 provide useful data for pharmacy research since this substance has been used as an oral vehicle to enhance compounds’ solubility [191, 192]. Authors found that both the emulsification and emulsion stability depended on which phase nanoparticles were initially dispersed, regardless of the surfactant used. When nanoparticles were first present in the oil phase, the emulsions’ stability was improved; if nanoparticles were added from the aqueous phase instead, no stabilization occurred due to repulsive electrostatic and hydration forces. At present, it seems mixtures of SiO_2 NPs and environmentally-friendly surfactants will be more relevant in cosmetics and drug formulations, as reported for lemongrass essential oil-in-water emulsions [193]. Specifically, the synergistic effect between the green surfactant PEG-4 Rapeseedamide and hydrophilic SiO_2 NPs impacted the rheological properties of the aforementioned emulsions, in which a significant increase in the elastic and viscous moduli was observed.

Additionally to O/W and W/O emulsions (simple emulsions), the combined effect of silica nanoparticles and nonionic surfactants has proven advantageous in pre-double emulsions formulation stabilization,

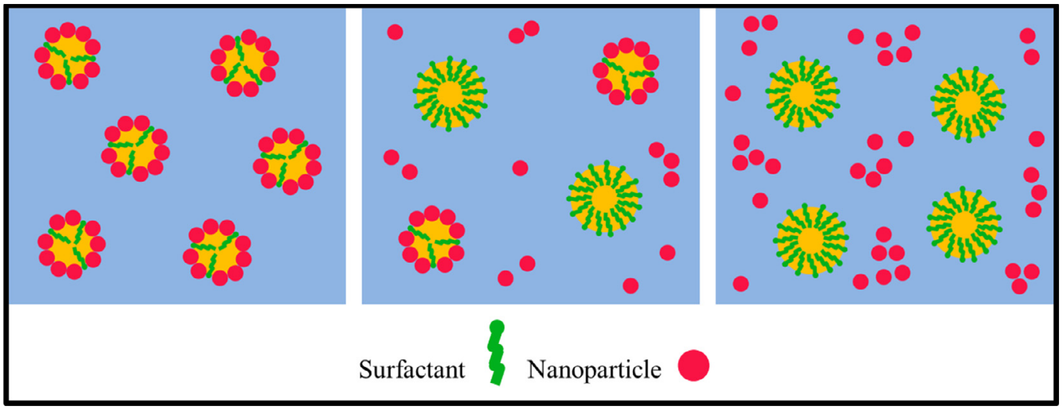


Fig. 10. Schematic representation of NPs displacement by surfactant in O/W emulsions according to [185]. Left: at low surfactant concentrations (0.4 wt%), both NPs and surfactant are adsorbed at the oil-water interface, and the oil droplet size is small. Center: at moderate surfactant concentrations (0.6 wt% and 1 wt%), some droplets are as those at lower surfactant concentrations, and others have no NPs at the interface (droplet size increases). Right: at higher surfactant concentration NPs at the oil-water interface have been totally replaced by surfactant. In the last two stages, NPs are displaced into the aqueous phase.

as stated by Wang et al. [194]. These emulsions, where rutin was chosen as a drug model, consisted of droplets of glycerol-rutin blends dispersed in evening primrose oil, which then were diluted in an aqueous medium. The double emulsions' great stability was attributed to the synergistic interaction between hydrophobic SiO_2 NPs and a nonionic surfactant (polyethylene glycol sorbitan monolaurate known as Tween 20, polyoxyethylene sorbitan monopalmitate known as Tween 40, Tween 60, polyethylene glycol sorbitan monooleate known as Tween 80, or macrogolglycerol hydroxystearate known as RH40). It is worthy to point out that in vitro experiments demonstrated that pre-double emulsions, where rutin was encapsulated, presented a higher skin permeation and drug distribution than rutin aqueous solutions. This investigation indicates that nonionic surfactant-SiO_2 NPs could play a significant role in the formulation of pre-double emulsions used as drug vehicles and, therefore, in the pharmaceutical and cosmetic industry.

It is relevant to mention that the industrial generation of emulsions may find a proper path in confined impinging jets (CIJs), a recent emulsification technique. This method has been used to prepare sunflower oil-in-water emulsion, whose interfaces were stabilized by mixtures of hydrophilic SiO_2 NPs and Tween 20 [195]. It was evidenced that emulsion stability predominantly depended on nanoparticle and surfactant concentrations, whereas CIJs operation conditions influenced droplet quantitative aspects. Energy-saving and the versatility to produce different emulsions formulation are some advantages of the CIJs technique that encourage more profound studies for its implementation.

5.4. *The case of bicontinuous emulsions*

So far in this manuscript, emulsions seen as droplet dispersions have been explored. Emulsions where two immiscible phases form percolating liquid domains in which interfaces are stabilized by particles exist and are called bicontinuous interfacially jammed emulsions gels (bijels) [196]. Since the first experimental report on bijels, more than a decade ago [197], different efforts have been carried out to obtain these materials, as their promising applications include cross-flow systems, scaffolds for catalysis, tissue engineering, and encapsulation-release [196].

Bijels were first obtained separating a binary liquid mixture via spinodal decomposition, stabilizing the two fluids channel's interfaces with neutrally wetted particles (contact angle $\approx 90^\circ$) [197-199]. This method, however, exhibits some limitations that bring problems in practice, such as a highly meticulous particle surface tuning to get a neutrally wetting behavior, the need for liquid mixtures which throughout spinodal decomposition separate into two liquid domains with approximately the same volume, a sufficiently fast quench rate that ensures spinodal decomposition (avoiding nucleation), and the hazardous character of one of the compounds of the mixtures usually used. Hence, these issues motivated the research of new bijel creation techniques involving SiO_2 NPs and surfactants.

A proposal to obtain bijels was developed based on solvent transfer-induced phase separation (STRIPS) [200]. In this method, hydrophilic SiO_2 NPs and CTAB are dispersed in a three-liquid mixture (Fig. 11a) containing ethanol, water, and oil (hexanedioldiacrylate, diethylphthalate, or butylacrylate). Then, this mixture is injected, using syringe pumps, into a glass capillary concentrically aligned in an external glass capillary. The continuous phase in the outer capillary is an aqueous CTAB solution that flows in the same direction as the internal mixture (Fig. 11b). As this operation proceeds, the solvent is extracted from the ternary mixture to the continuous phase. This causes a phase separation through spinodal decomposition, and a bicontinuous structure stabilized by particles attached at the interfaces is produced. Precisely, hydrophilic SiO_2 NPs are dispersed in the ternary mixture, which contains an amount of CTAB, and, as stated in previous sections, the surfactant adsorbs onto the surface of the nanoparticles by electrostatic interactions and partially increases their hydrophobicity. Therefore, nanoparticles anchor at oil-water interfaces, arresting the phase separation and stabilizing the bicontinuous emulsion formed. Fig. 11a–f shows the essential features involved in the STRIPS method. It was later reported that the stability of STRIPS bijels could be achieved by choosing the appropriate combination between silica nanoparticles' wettability and the surfactant structure [201]. Although acrylate-functionalized nanoparticles (partially hydrophobic nanoparticles) stabilize STRIPS bijels, a marked enhancement on the bijel stability is observed when dodecyltrimethylammonium bromide (C_{12}TAB) is added. On the other hand, nanoparticles containing 3-glycidoxy-propyl-trimethoxysilane groups (strongly hydrophilic nanoparticles) required a double chain surfactant (dihexadecyl dimethylammonium bromide ($(C_{16})_2$TAB) to stabilize the bijel.

In a subsequent study, bijels were successfully prepared following a two-step mixing protocol for a glycerol-silicon oil system containing silica nanoparticles and CTAB [202]. During mixing, droplets of one of the liquids are generated, and the interfacial nanoparticle concentration will drive either spherical or non-spherical droplets. As mixing continues, droplets are distorted and then break up to arrange into a domain network. Once the nanoparticles' contact angle is modified by the surfactant adsorption on their surface, SiO_2 NPs stabilize the created liquid domains' interfaces. In Fig. 11g a confocal image of the bijel obtained by mixing is observed, and the bicontinuous interconnected structure can be distinguished. Additionally to a correct mixing procedure and a proper amount of CTAB to modify the silica nanoparticles' wettability, the high viscosity of the liquids used is an important parameter since it contributes to slow down the system dynamics.

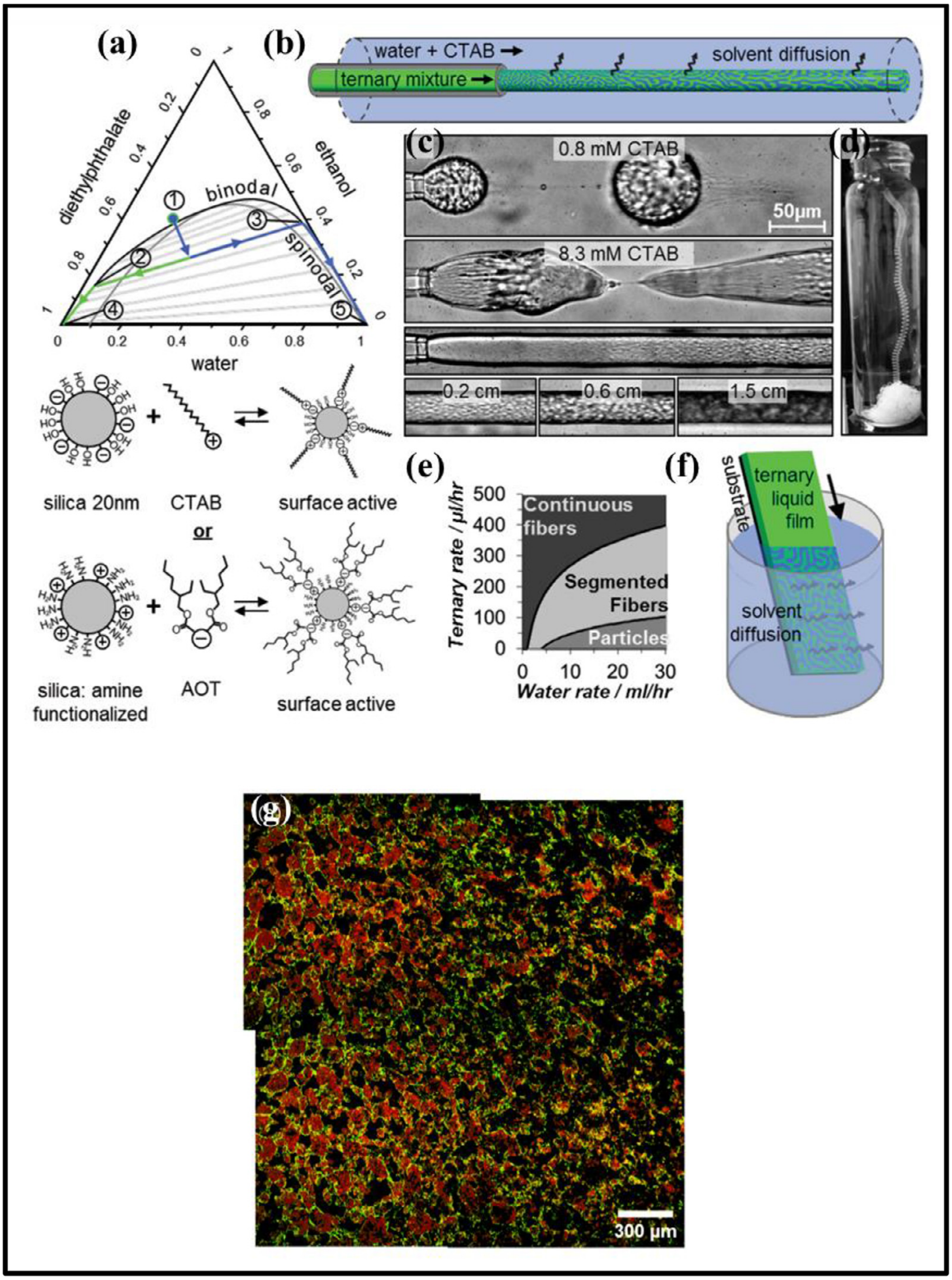


Fig. 11. Bijel structure formation via STRIPS. (a) Equilibrium phase diagram of the ternary liquid system comprising diethyl phthalate (DEP), ethanol, and water (volume fractions). Arrows qualitatively depict the average compositional path, initiating at point 1 as a homogeneous ternary liquid mixture, progressing to points 2 and 3, and eventually to points 4 and 5 as the mixture phase separates due to ethanol loss and water uptake. The scheme of the surface modification of silica nanoparticles by CTAB or amine-functionalized silica by docusate sodium salt (AOT) is presented below the phase diagram. (b) Representation of bijel fiber formation in a device made of concentrically aligned glass capillaries (diameters = 50 and 300 μm): The ternary liquid mixture containing CTAB and suspended nanoparticles flows like a jet from a nozzle into a water stream of pH 3 containing CTAB 1×10^{-3} M. (c) Images of bijel microparticle and bijel fiber formation: high-speed images of the ternary droplet-pinch off at low CTAB concentration, 0.8×10^{-3} M, in the ternary mixture. The image below shows the pinch-off at elevated CTAB concentration, 8.3×10^{-3} M, in the ternary mixture. Liquid jet at a high flow rate of the ternary mixture (300 $\mu L\ h^{-1}$) and after polydiallyldimethylammonium chloride surface modification of the capillary. Below: images of the jet at different longitudinal positions. (d) Photograph of the collection of a continuous bijel fiber flowing out of the microfluidic device. (e) Operation diagram showing the effect of flow rate on the bijel structure formed in the capillary device. (f) Representation of bijel membrane formation: a hydrophobic substrate is coated with a thin film of the CTAB and silica doped ternary mixture and afterward immersed into a water bath. (Reproduced with permission [200] Copyright 2015, John Wiley and Sons). (g) A mosaic of four confocal micrographs taken close together and aligned to show the morphology on a several millimeters scale. The green is the fluorescein isothiocyanate (FITC) labeled nanoparticles and red is the Nile Red labeled glycerol. (Reproduced with permission [202] Copyright 2017, The Royal Society of Chemistry).

Table 1
Summary of the different SiO_2 NPs-surfactant pairs used on the stabilization of foams.

Research field	NPs type	Surfactant type	References
EOR	Hydrophilic	Cationic (single-tailed, double-tailed, gemini)	[112–118,122]
		Zwitterionic	[119–122,135]
		Short compound	[123–125]
		Anionic	[29,84,86,117,118,122, 127–132,135,139]
		Nonionic	[99,105,118,122]
	Hydrophobic and partially hydrophobic	Anionic	[29,34,35,95,97,126, 127,129,130,133,138]
Responsive systems and novel formulations	Hydrophilic	Cationic	[144,150]
		Anionic	[146,147]
		Zwitterionic	[145]
	Hydrophobic and partially hydrophobic	Anionic	[146,147]
		Fatty acid	[38]
Macroporous materials	Hydrophilic	Short compounds	[123,151,152]
	Hydrophobic and partially hydrophobic		Not reported

Table 2
Summary of the different SiO_2 NPs-surfactant pairs used on the stabilization of emulsions.

Research field	NPs type	Surfactant type	References
EOR	Hydrophilic	Cationic	[89,158,159]
		Anionic	[89,159,160]
		Nonionic	[159]
	Hydrophobic and partially hydrophobic	Anionic	[98]
Responsive systems	Hydrophilic	Cationic	[166–171]
		Zwitterionic and switchable	[172–174]
		Nonionic	[175–177]
	Hydrophobic and partially hydrophobic	Nonionic	[176–177]
		Anionic	[178,179]
Macroporous materials	Hydrophilic	Cationic	[36]
		Short compounds	[37,183]
	Hydrophobic and partially hydrophobic	Nonionic	[106]
Food and pharmaceutical engineering	Hydrophilic	Nonionic	[39,185,188,193–195]
		Cationic, anionic	[190]
	Hydrophobic and partially hydrophobic	Nonionic	[186–189]
Bijels elaboration	Hydrophilic	Cationic	[200–202]
	Hydrophobic and partially hydrophobic	Cationic	[201]

The final choice of a bijel elaboration's method will certainly rely on the material's ultimate application and the laboratory facilities. With the STRIPS method, it is possible to fabricate bijel microparticles, fibers, and membranes [200]. However, the mixing technique offers bijel production without the restraints of phase diagrams, and a practical means to study the rheological properties of the bicontinuous emulsion produced [203].

6. Summary of the systems discussed

Summaries of the foams and emulsions revised in this manuscript are presented in Tables 1 and 2, respectively. Tables include the different research fields where both systems are studied. It is observed that hydrophilic SiO_2 NPs are preferred over hydrophobic NPs or with a certain degree of hydrophobicity. This is most probably linked with the fact that SiO_2 NPs are hydrophilic in the natural form. Then, to obtain hydrophobic SiO_2 NPs, surface modification reactions and purification routes are required. Tables 1 and 2, together with the information in Section 2 of this manuscript, allow establishing a general rule in selecting SiO_2 NPs-surfactant pairs to achieve a good synergistic effect. Cationic surfactants, as well as zwitterionic and alkylamines, are usually chosen to mix with hydrophilic SiO_2 NPs, which is related to electrostatic interactions. On the other hand, anionic surfactants are mainly employed with hydrophobic (or partially hydrophobic) SiO_2 NPs due to hydrophobic interactions. Of course, exceptions to this rule are found depending on the application context, for example, oil reservoir conditions. Regarding nonionic surfactants, especially the case of “food-grade” and potential pharmaceutical emulsions, experiments with either hydrophilic or hydrophobic SiO_2 NPs are performed.

7. Conclusions

Abundant evidence of the stabilization of aqueous foams and emulsions by the combined action of silica nanoparticles and surfactants was given in this review. In the last decade, surfactant molecules adsorption on silica nanoparticle surfaces has been claimed as a practical and non-expensive route to modify silica nanoparticles' wettability to stabilize bubbles and droplets. Certainly, mixtures of silica nanoparticles with cationic, zwitterionic, anionic, or nonionic surfactants contribute to enhance foams and emulsions lifetime; however, from the reports here reviewed, it can be assumed that the best synergistic effect will mainly depend on the interactions between the selected silica nanoparticle-surfactant pair.

Throughout these pages, it was clear that most of the foams and emulsions revised are directly linked to applications in different process engineering areas. The elaboration of macroporous materials and the formulation of responsive systems definitely have an impact on materials engineering; the injection of SiO_2 NPs-surfactants stabilized foams and emulsions into laboratory-made, or pilot scale oil reservoirs is of interest in petroleum engineering; single and pre-double emulsions used as drug carriers attracted attention in the pharmaceutical manufacturing, and "food-grade" emulsions became promising systems in food engineering.

One can envisage that the number and applications of foams and emulsions stabilized by silica nanoparticles and surfactant mixtures will increase in the near future, although their final implementation in industrial processes will depend on their toxicological, environmental, and economic scrutiny. Ultrastable foams and emulsions at high temperatures, switchable systems, foams to liquid marbles transitions, crude oil emulsions, and bijels, are some of the current and future research lines that will surely strengthen. Indeed, novel synthesis of surfactants and chemical modifications of silica nanoparticles' surface will also be relevant for the formulation of foams and emulsions containing both stabilizers.

A few reviews on mixtures of nanoparticles and surfactants stabilizing emulsions and foams are found in the literature, although, to the best of our knowledge, this is the first one focused only on silica nanoparticles and surfactants. We undoubtedly think this review offers valuable information, as silica nanoparticles are largely used in both laboratories and industry.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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