Effect of Silica Particles on Stability of Highly Concentrated Water-In-Oil Emulsions with Non-Ionic Surfactant[1]

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Abstract—Water-in-oil, high internal phase emulsion made of super-cooled aqueous solution containing a mixture of inorganic salts and stabilized with non-ionic surfactant (sorbitan monooleate) alone was investigated. It was not possible to produce a highly concentrated emulsion (with aqueous phase fraction = 94 wt %), stabilized with surface-treated silica, solely: we were able to form an emulsion with a maximal aqueous phase mass fraction of 85 wt % (emulsion inverts/breaks above this concentration). The inversion point is dependent on the silica particle concentration, presence of salt in the aqueous phase, and does not depend on the pH of the dispersed phase. All emulsions stabilized by the nanoparticles solely were unstable to shear. So, the rheological properties and stability of the emulsions containing super-cooled dispersed phase, with regards to crystallization, were determined for an emulsion stabilized by non-ionic surfactant only. The results were compared to the properties obtained for emulsions stabilized by surface treated (relatively hydrophobic) silica nanoparticles as a co-surfactant to sorbitan monooleate. The influence of the particle concentration, type of silica surface treatment, particle/surfactant ratio on emulsification and emulsion rheological properties was studied. The presence of the particles as a co-stabilizer increases the stability of all emulsions. Also, it was found that the particle/surfactant ratio is important since the most stable emulsions are those where particles dominate over the surfactant, when the surfactant's role is to create bridging flocculation of the particles. The combination of the two types of hydrophobic silica particles as co-surfactants is: one that resides at the water/oil interface and provides a steric boundary and another that remains in the oil phase creating a 3D-network throughout the oil phase, which is even more beneficiary in terms of the emulsion stability.

INTRODUCTION

Some commercially available, highly concentrated emulsion compositions comprise of an external organic oil phase in which an aqueous solution of an inorganic salt is dispersed [1–3]. The water content of the dispersed phase (DPh) can be reduced by a factor of 10–20%, by weight of the emulsion aqueous phase. This means that the DPH is in a metastable or super-cooled state and therefore exhibits a tendency to crystallize.

The ability of conventional surfactants to stabilize emulsions has long been appreciated [4]. The stability of a high internal phase emulsion (HIPE) composition is affected in the presence of modifying emulsifiers that first promote the subdivision of the dispersed droplets; and additionally, by covering the water/oil interface, reduce the break-down of the emulsion by inhibiting coalescence and agglomeration of the droplets. A number of attempts have been made at trying to improve the shelf-life of the HIPE and these attempts were mainly concentrated on the selection of a suitable conventional surfactant composition, which was de-signed to minimize the coalescence of the supersaturated droplets of the inorganic salt solution of the DPh [5].

In the last two decades, solid particles stabilized or Pickering emulsions have become of great interest in many industries such as food, pharmaceutical, cosmetic, etc., due to the particle stabilization difference when compared to conventional surfactant stabilization [6–9]. For example, besides the similarities between colloidal particles and conventional surfactant stabilization, colloidal particles adsorb more strongly at the water/oil interface and once adsorbed cannot easily be removed from the interface by other amphiphiles [10–12], or during intensive processing, whereby a more rigid interface is formed [13]. Moreover, they are able to form a steric boundary which is responsible for emulsion stabilization when a 2D network is formed at the interface (the strength of the particle aggregation prevents displacement at the interface) [14]. It has also been reported that when a 3D network is formed, it extends the particle network throughout the continuous phase, thus improving stability by preventing droplet-droplet contact [14]. But despite such great interest, not much literature is avail-
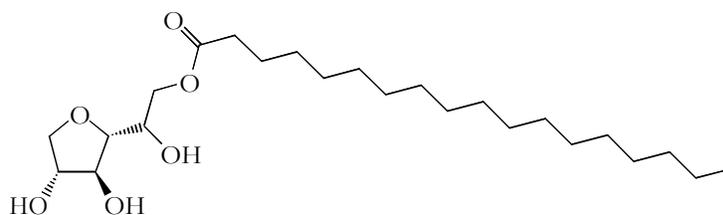
Fig. 1. Chemical structure of sorbitan monooleate.

able with regards to HIPEs or emulsions where the volume fraction exceeds the maximum packing fraction for monodispersed spheres, which are widely used in different industries. Moreover, it has been reported that it is not possible to form the Pickering emulsion with a DPh volume fraction higher than 0.71 [15–17].

The need has arisen to make use of the advantages associated with surfactant and particles stabilized emulsions in order to eliminate the disadvantages of their individual use as sole components and to produce stable HIPEs. Little or no interest has been given to the use of emulsions, where combinations of surfactants and particles are used, with regards to HIPEs [18–21]. However, it was deduced that there is an increase in the stability of oil-in-water emulsions when the mixed system is used [20, 13].

The study presented herein deals with water-in-oil HIPEs, where the DPh is a supersaturated aqueous solution of inorganic salts [22–24]. To better understand the role of the particles in stabilization of emulsions against the aqueous phase crystallization, the emulsion formation refinement time to form an emulsion with constant droplet size as well as the rheological properties were determined, in order to compare them with the properties of emulsions stabilized by non-ionic emulsifiers solely.
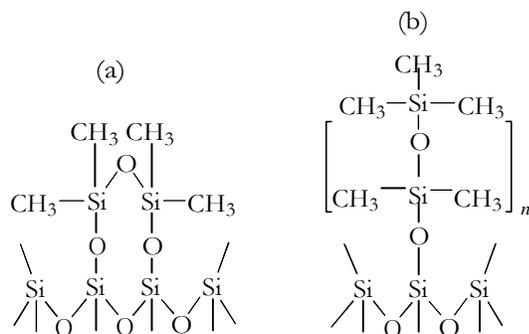
Fig. 2. Structure of fumed silica: (a) CAB-O-SIL® TS 610 silica which has been treated with dimethyldichlorosilane; (b) CAB-O-SIL® TS 720 silica which has been treated with polydimethylsiloxane.

EXPERIMENTAL

Materials

The oil used was industrial grade hydrocarbon oil that had a density of 0.795 kg/L (at 20°C), a kinematic viscosity of 2.9 cSt (at 40°C), an aromatic content of 8% and a flash point of 98°C. Deionized water, purified with "Milli-Q" system, was used in all the experiments. The lipophilic nonionic surfactant sorbitan monooleate (SMO) that was used was supplied by Lake International Co. (Republic of South Africa). The chemical structure of SMO is presented in Fig. 1. The particles used are fumed silica of the CAB-O-SIL® range (CAB-O-SIL® TS 610 and CAB-O-SIL® TS 720) from CABOT Corp. (USA). They consist of aggregates (0.2–0.3 μm) obtained by fusion of primary spheres (sphere surface area 105–140 m²/g) by hydrogen bonding between hydroxyl groups. The silica nanoparticles belong to treated type particles where the amphiphility depends on the type and degree of treatment. The treatment replaces some of the hydroxyls on the surface of the silica thus resulting in increased hydrophobicity. Both particles used in this study are lipophilic, where CAB-O-SIL® TS 610 is less lipophilic than CAB-O-SIL® TS 720. The structure of the silica particles used for the investigation is presented in Fig. 2.

The emulsion was prepared using a solution of surfactants in hydrocarbon oil and aqueous solution of inorganic salts. Water comprises app. 20% by weight of the solution. The crystallisation temperature (fudge point) of the inorganic salt solution is app. 59°C. The density of the aqueous solution is 1.4 to 1.5 kg/L. The oil phase mass fraction is kept at 6% of the total mass of the emulsions that were investigated. The oil phase was prepared by mixing the emulsifier and/or nanoparticles with hydrocarbon oil by means of an Ultra Turrax T25 stirrer (Jannke&Kuntel, Germany) at 3000 rpm for 15 min at ambient temperature. For the preparation of the emulsion DPh, a mixture of granulated inorganic salts was dissolved in water at a temperature of 80°C. The concentration of the salts in the aqueous solution was kept at 80 wt % and controlled by the fudge point. To prepare emulsion samples, the Hobart mixing technique was used. The emulsion was made at 80°C by the incorporation of the aqueous phase into the oil phase. After complete addition of the

aqueous phase, the stirring was maintained for different periods of time, but at the same speed of agitator, in order to prepare the samples with the same droplet sizes but different oil phase content. The emulsion was stored at ambient temperature. In order to study the effect of silica nanoparticles on the stability of water-in-oil emulsions, the emulsion was prepared by slowly adding a known amount of 60 wt % aqueous solution of inorganic salts to the oil phase, while mixing the system using the Ultra Turrax T25 stirrer at 3000 rpm at ambient temperature.

Methods

Droplet size determination. The droplet size distributions were measured using a Malvern Mastersizer 2000 instrument. The procedure is based on sample dispersion under software control and the measurement of angle dependence of the intensity of scattering of a collimated He-Ne laser beam. The particle size distribution calculations are based on the rigorous Mie theory and using the standard software applied to the instrument. The sample was diluted in the oil of the continuous phase just before the measurements were taken.

Rheology. The basic rheological measurements were carried out with the use of a rotational dynamic rheometer MCR 300 (Paar Physica). The geometry of the measuring unit was "bob-in-cup" (coaxial cylinder with conical base to the bob) with sandblasted bob surface. The bob diameter was 27 mm and the gap distance between the cup and the bob was 1 mm. Two different regimes of deformation were used: (i) steady state flow measuring flow curves (shear stress versus shear rate); (ii) oscillatory measurements for measuring strain amplitude dependencies of the storage component of dynamic modulus. All the rheological measurements were conducted at 30°C.

RESULTS AND DISCUSSION

Emulsion Stabilized Solely by Classic Surfactant

The stability of water-in-oil, high internal phase emulsions (HIPEs) is mainly associated with the crystallization of the super-cooled DPh: no coalescence of this phase is observed during emulsion ageing; in other words, crystallisation of the DPh comes first. Therefore, in this work, the term "emulsion stability" would refer to the emulsion stability when compared to crystallisation of emulsions made with the super-cooled DPh, unless otherwise stated. Thus, emulsion can be formed and remains stable for some period of time when stabilized by SMO only, but the shelf-life of the emulsion is affected by the amount of emulsifier presented in the emulsion. Higher concentrations of SMO in the emulsion oil phase destabilize emulsion (see Table 1).

At SMO concentration of 14.0 wt % there was clear decrease in refinement time to produce an emulsion

Table 1. Emulsion properties as a function of SMO concentration

| C_{SMO} in oil phase, wt %	Refinement time ($D = 10$ μm)	Stability, days	τ_y, Pa	G_0, Pa
14.0	35 s	10	6	311
5.0	5 min	29	9	526

with an average droplet size D of 10 μm, as presented in Table 1. The rheological properties of the emulsions are also affected by the amount surfactant present. As is evident from Fig. 3, the character of the flow behavior is not affected by the concentration of SMO in the oil phase, but with an increase of the emulsifier concentration, the flow curves shift to the lower shear stresses over the whole range of shear rates. Both samples conformed well to the Herschel–Bulkley model:

$\tau = \tau_y + K\dot{\gamma}^n$, where τ_y is the apparent yield stress. The yield stress values were determined using this model. The oscillatory experimental results are shown in Fig. 4 for all the SMO concentrations that were studied; a plateau zone (G_0) appears for the G' value. The recording of the elastic parameter (G') in the linear region shows a decrease of G_0 when the surfactant concentration increases, indicating some changes.

The aforementioned observations are not surprising since SMO is known to form interfacial arrangements due to the interfacial multilayer formation [25, 26]. The buildup structure makes the interface progressively opaque, thus affecting the shelf-life of emulsions, as well as the rheological properties. Such structures are more pronounced in the presence of emulsifier excess [25], which is in accordance with this experiment.

Shear stress, Pa
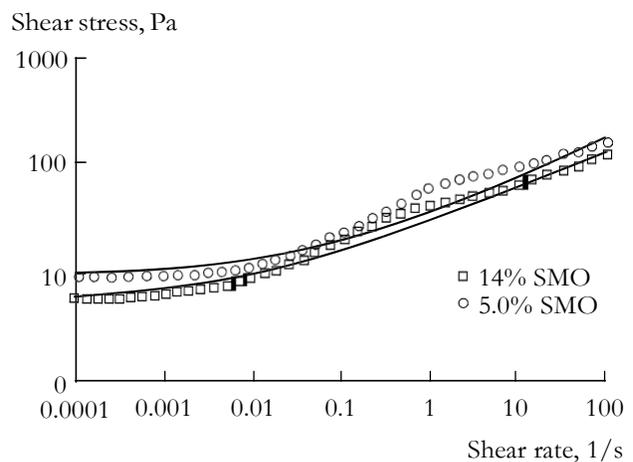
Fig. 3. Effect of SMO concentration on flow behavior.
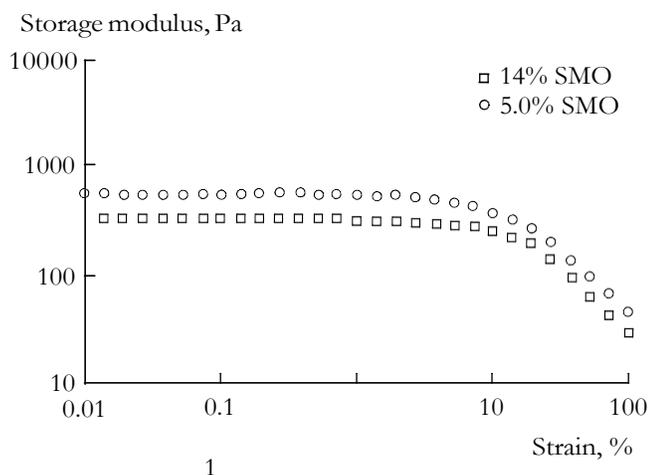
Storage modulus, Pa

**Fig. 4.** Effect of concentration of SMO in oil phase on storage modulus.

Emulsion Stabilized Solely by Silica Nanoparticles

The ability of silica particles to stabilize water-in-oil, high internal phase emulsions as a function of type of particle surface treatment (CAB-O-SIL TS610—less hydrophobic or TS720—more hydrophobic); particle concentration; pH of dispersed phase; and salt presence in aqueous phase has been studied. It was not possible to form HIPE (94 wt % of dispersed phase): (i) it was not possible to produce any emulsion using CAB-O-SIL TS720 silica; (ii) using CAB-O-SIL TS610 silica the emulsion inverts/breaks at some point; (iii) emulsions are shear unstable according to the simple "hand shear" test and dynamic light scattering results, and therefore it was not possible to measure any properties involving shear, such as droplet size and size distribution or rheological properties. However, having demonstrated in this section the properties of emulsions stabilized by silica nanoparticles solely, we aim to further show the advantages of using silica, together with SMO (conventional surfactant), as an emulsion stabilizing mixture.

In this part, the investigations focused predominantly on the stability in terms of the whether it was possible to form water-in-oil HIPEs, and the measure of such stability was categorised by the point at which emulsion inverts to a less stable water-in-oil type or breaks.

Table 2. Effect of silica content in oil phase on emulsion stability

C_{silica}, wt %	$C_{DPh}^{Inversion}$, wt %	Sedimentation (80% DPh)
1	79	yes (8 days)
2	83	no (6 months)
3	85	no (6 months)
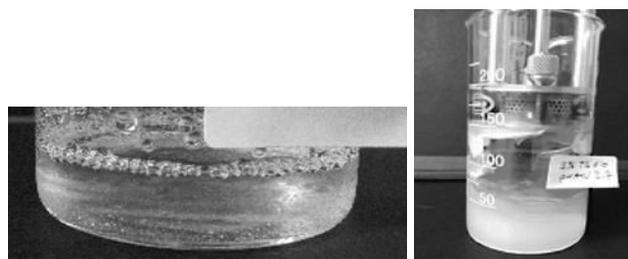
Fig. 5. (a) Emulsion is not formed when CAB-O-SIL TS720 is used as stabilizer; (b) emulsion is formed when CAB-O-SIL TS610 is used as stabilizer.

The effect of the silica particle treatment or the extension of hydrophobicity on emulsion stability was initially investigated. It was found that in the obtained emulsion system, more hydrophobic CAB-O-SIL TS720 particles are not surface active and remain in the oil phase thus preventing the formation of an emulsion using CAB-O-SIL TS720 particles as a stabilizer solely, whereas less hydrophobic CAB-O-SIL TS610 particles can stabilize and are therefore able to produce an emulsion (Fig. 5). Thus, for further investigation, CAB-O-SIL TS610 particles have been chosen.

The stability of emulsions that were stabilized by silica particles, as a function of aqueous phase composition and pH, was also investigated. It was found that the presence of inorganic salts in the DPh moves the inversion point to higher concentrations. For example, for pure water as a DPh its value is 77 wt %, whereas for emulsions containing 60% inorganic salt solution as the aqueous phase the value is 84 wt %. The effect is clear from the point of view that the presence of electrolytes in the aqueous phase may affect the particle position at the interface by affecting the water-liking groups of silica. It is known that the pH of the aqueous phase may affect the position of particles at an interface or can change the particle wettability as well by the ionization of water-active groups [27]. But in this case the pH effect was disguised by the presence of a large amount of electrolytes in the aqueous phase (60% inorganic salts aqueous solution) of the emulsion.

The effect of the concentration of silica particles on the ability to form HIPE was also studied. The concentration of colloidal particles was varied from 1 to 3 wt % in the oil phase (in 1% increments) and the emulsion stability was judged by determining the inversion point and the stability with regards to sedimentation (Table 2). The concentration of the particles was found to affect the emulsion stability. This is particularly apparent with an increase in the concentration of CAB-O-SIL TS610 in the system, whereby a denser 3D network is formed, thus increasing the emulsion viscosity and shifting the inversion point of the emulsion to a higher DPh mass fraction, plus it also increased the stability with regards to sedimenta-
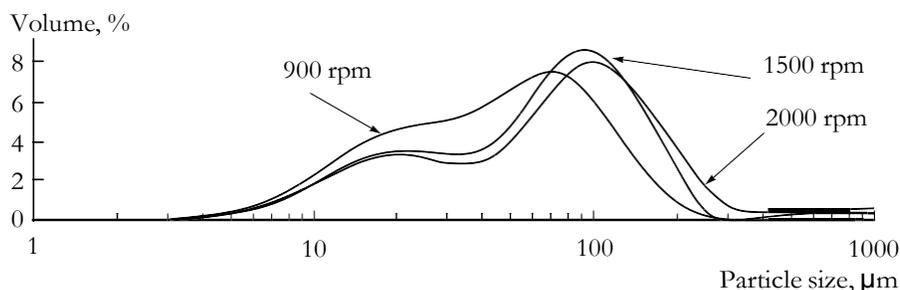
Fig. 6. Droplet size measurement results, increased speed of agitation.

tion. The stability to sedimentation was studied based on emulsions characterized by a DPh mass fraction of 80% (Table 2).

However, a condensed 3D structure formed when the emulsion was stabilized by silica particles solely, resulting in a shear unstable emulsion that is possibly caused by the high rigidity of the particle-formed structure that prevents interface stretching. The shear instability was detected by a simple "hand shear" test, whereby a small amount of emulsion is placed on the palm and sheared by the finger. The changes in droplet size and size distribution diagram at an increased speed of agitation during droplet size measurements can also be used as evidence of such shear instability (Fig. 6).

Emulsion Stabilized by Binary Surfactant Mixture: Conventional Surfactant plus Silica Nanoparticles
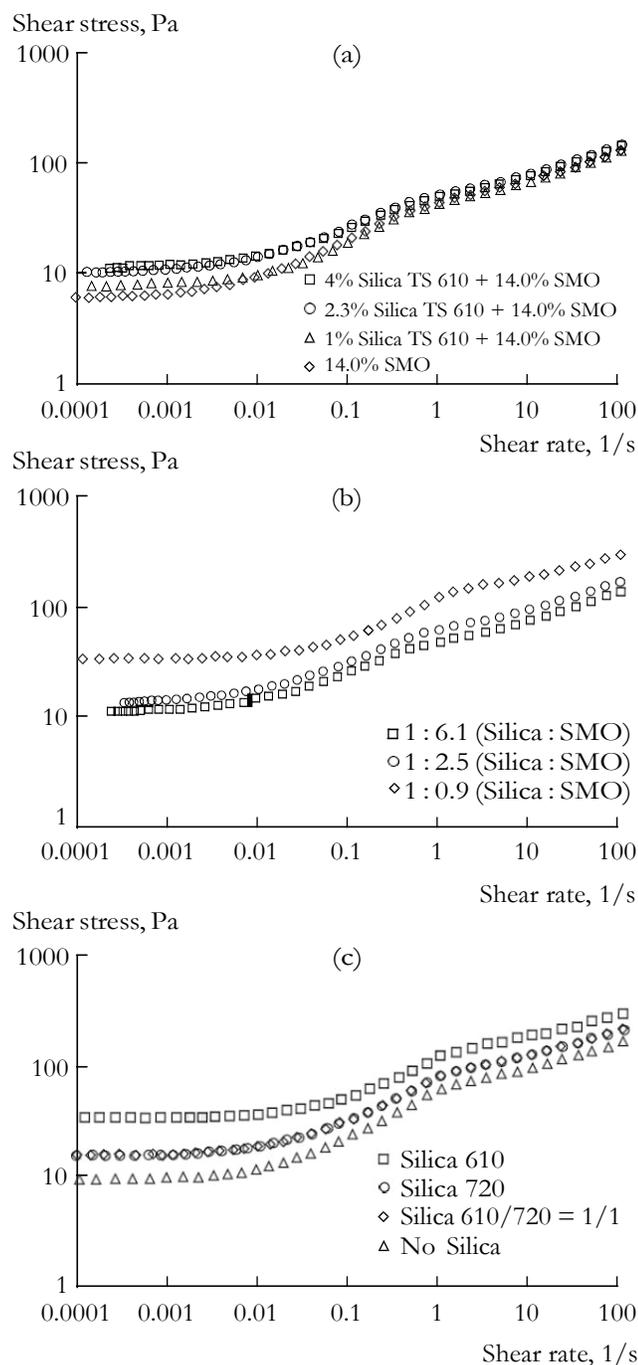
The stability of water-in-oil HIPEs containing both conventional non-ionic surfactant and silica nanoparticles was investigated. The concentration of

SMO was varied from 1.25 to 14 wt % in oil phase whereas the amount of colloidal particles was varied from 1.0 to 5.7 wt %. The mass fraction of DPh, as well as the average droplet diameter, was kept constant in order to minimize the number of variables. The stability was judged visually by detecting the starting point of the emulsion dispersed phase crystallization. The rheological properties, as well as the emulsification time that is required to produce emulsions with the same droplet size, were studied as a function of the silica nanoparticle concentration, the nanoparticle to SMO ratio and the particle hydrophobicity.

Table 3 and Figs. 7 and 8 summarize the test results for all the emulsion groups that were investigated. There were three groups that were studied: the first one is named "*Effect of silica concentration*", whereby the concentration of CAB-O-SIL TS 610 silica (less hydrophobic one) was varied from 0 to 4 wt % keeping the SMO concentration in oil constant at 14.0 wt %; the second one named "*Effect of CAB-O-SIL TS 610 silica to SMO ratio*" where the silica : SMO ratio was changed from 1 : 6.1 to 1 : 0.9; and the third one
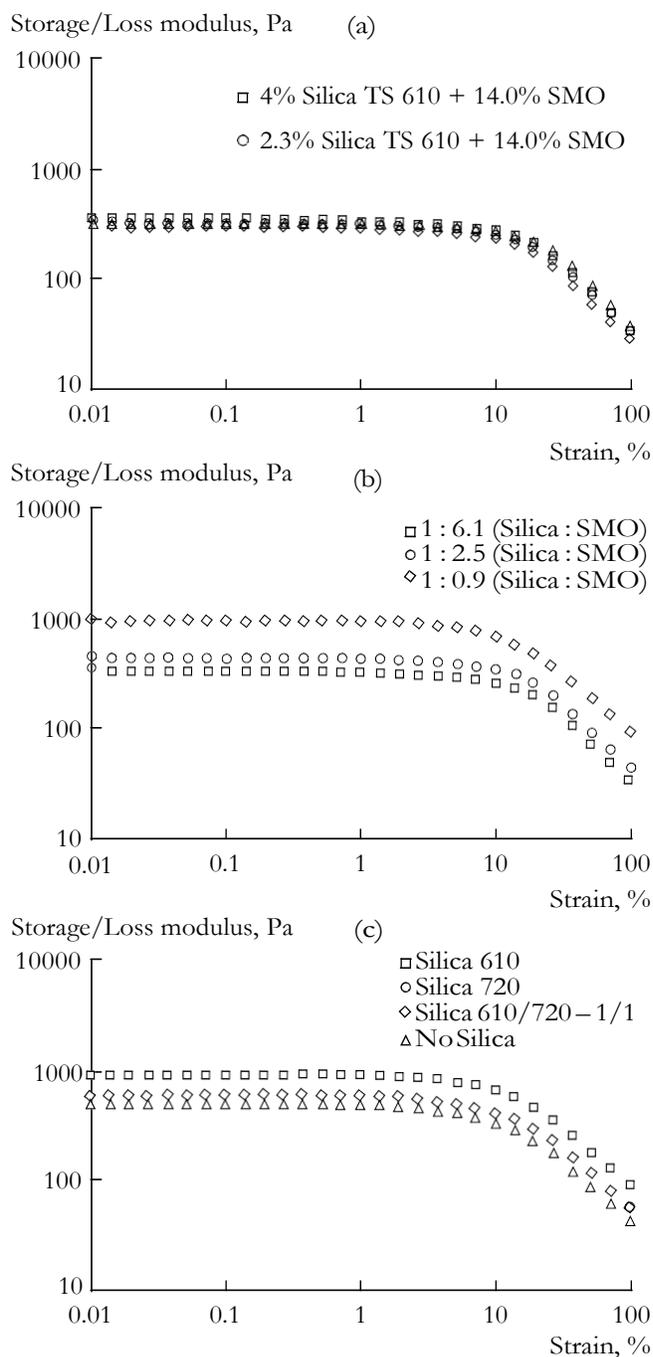
Table 3. Summarized effects on emulsion stability and properties

C_{silica} in oil phase, wt%	C_{SMO} in oil phase, wt%	Refinement time ($D = 10$ μm)	Stability, days	τ_y, Pa	G_0, Pa
Effect of CAB-O-SIL TS 610 silica concentration (constant SMO concentration – 14.0%)					
4.0	14.0	25 s	14	10	337
2.3	14.0	30 s	14	11	363
1.0	14.0	30 s	14	7	327
0	14.0	35 s	10	6	311
Effect of CAB-O-SIL TS 610 silica/SMO ratio					
2.3 (1)	14 (6.1)	30 s	14	11	363
4.0 (1)	9.8 (2.5)	60 s	16	13	440
5.7 (1)	5.0 (0.9)	15 min	50	33	980
Effect of silica hydrophobicity (constant SMO concentration – 5.0%)					
5.7 (TS610)	5.0	15 min	50	33	980
5.7 (TS720)	5.0	3 min	50	15	625
5.7 (720/610)	5.0	3 min	60	15	625
0	5.0	5 min	29	9	526

Fig. 7. Effect of: (a) concentration of TS 610 silica at constant concentration of SMO; (b) silica/SMO ratio at constant total concentration of surfactants; and (c) silica hydrophobicity on flow behavior.
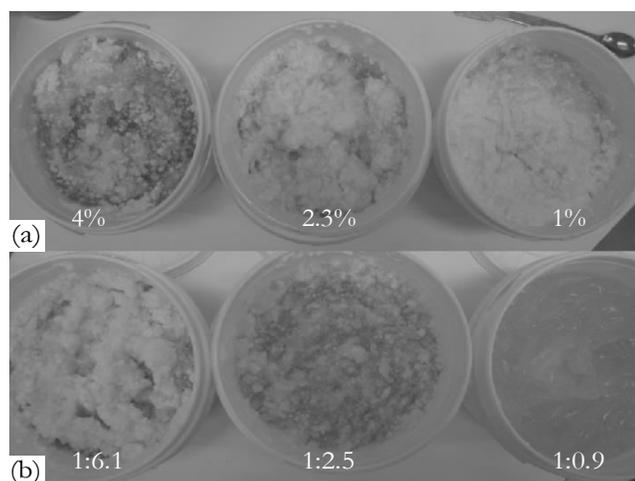

Fig. 8. Effect of: (a) concentration of TS 610 silica at constant concentration of SMO; (b) silica/SMO ratio at constant total concentration of surfactants; and (c) silica hydrophobicity on storage modulus.

named "*Effect of silica hydrophobicity*", whereby the concentrations of both stabilizers were not changed, but the hydrophobicity of silica added to SMO was varied from the less hydrophobic TS 610 to an average hydrophobicity of silica (TS 720/TS 610), obtained by mixing the two types of particles in a 1 : 1 ratio and then to the most hydrophobic one (TS 720). The re-

sults where compared with those for the emulsions stabilized by conventional surfactant.

On the basis of the above experimental results, it can be suggested that when there is an excess of conventional non-ionic surfactant (14.0 wt % in oil phase) no major changes in any data was obtained: the emulsification time was almost the same, the rheological

Fig. 9. Photographs of buckets containing emulsions at 30 days of ageing. Effect of: (a) concentration of TS 610 silica at constant concentration of SMO; and (b) silica/SMO ratio at constant total concentration of surfactants.

Fig. 10. Illustration of suggested interface and oil phase structure (a) in excess of conventional non-ionic surfactant; and (b) at optimal combination/ratio of particles and surfactant.

parameters (yield point and plateau modulus) increased slightly with an increase in the nanoparticle concentration (Table 3, Figs. 7a, 8a) and the starting point of the emulsion DPh crystallization improved slightly, however the stability in terms of the crystallization rate was much improved (Fig. 9a). The picture changes when the colloidal particles start to dominate over the SMO (Table 3, Figs. 7b, 8b and 9b), and this is clearly observed when the total surfactant concentration is kept constant and the silica/SMO ratio is varied. For emulsions stabilized by 5.7 wt % of silica and 5.0 wt % of SMO the rheological characteristics drastically increased, and the stability was greatly enhanced when compared to emulsion that was stabilized by 2.3 wt % of silica and 14.0 wt % of SMO. The effect could be summarized as the following: (i) a synergistic effect was exhibited between the silica nanoparticles and the SMO; (ii) when an excess of conventional surfactant is present, there is too much surfactant and this excess surfactant may be adsorbed onto the particles, making them too hydrophobic to be able to reside at the water/oil interface. In excess of SMO, when there is a lot of "free" (unattached to silica) surfactant, it covers the water/oil interface before nanoparticles do (Fig. 10a). The slightly improved stability effect was probably observed due to a 3D network created by the particles in the oil phase that slowed the formation of the opaque multilayer of SMO at the water/oil interface (see *Emulsion Stabilized Solely by Classic Surfactant* part); (iii) emulsion stability can be remarkably enhanced by optimization of the combination or ratio of the particles and the surfactant (Fig. 10b), whereas the role of SMO is also important in terms of promoting the nanoparticles' flocculation, thus providing a less rigid particle structure that is
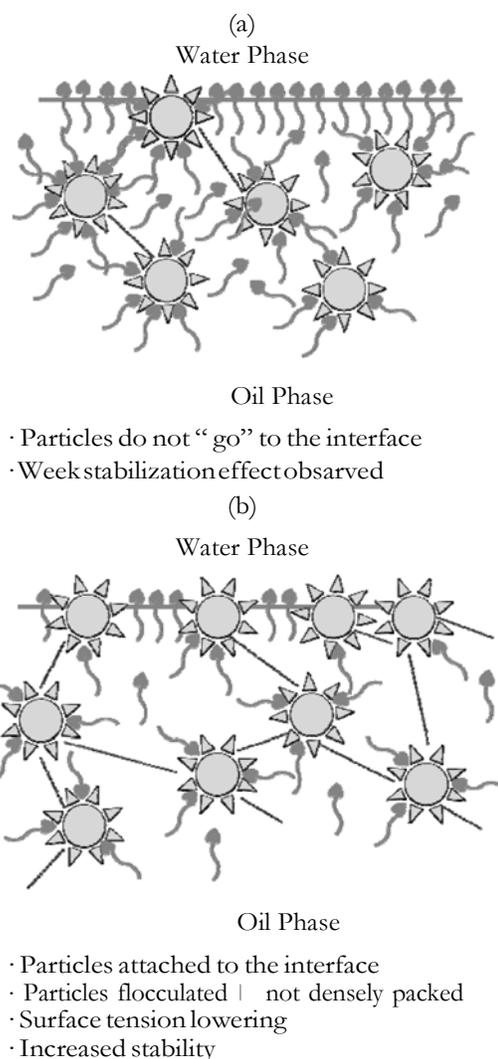
more stable to stretching, helping to render the particle wettability and lowering the interfacial tension.

Moreover, based on the results in Table 3, the input of the combination of relatively less hydrophobic CAB-O-SIL TS 610 silica and relatively more hydrophobic CAB-O-SIL TS 720 silica as a co-surfactant to the conventional non-ionic emulsifier SMO was more pronounced in terms of long-life emulsion stability, when compared to emulsion stabilized by one type of nanoparticles. The effect could possibly be understood from the following point of view: the increased stability is related to the presence of one type of colloidal particles (CAB-O-SIL TS 610) or their arrangements at the water/oil interface, creating a "protective shell" for droplets; whereas nanoparticles of another type (CAB-O-SIL TS 720) remain in the oil phase provid-

ing a three-dimensional network among the protected droplets and particles.

CONCLUSIONS

A detailed investigation of the stability in terms of the crystallization of the dispersed phase of high internal phase water-in-oil emulsions, stabilized by conventional non-ionic surfactant (SMO) solely or by surface-active silica nanoparticles only, as well as by their mixtures, has been done. Neither silica nanoparticles nor the SMO surfactant in the absence of each other produces a stable emulsion within our experimental window. It was demonstrated that emulsions are more stable when prepared from a flocculated dispersion as an oil phase. Therefore, the oil phase for the emulsions stabilized by a mixture of SMO and silica was prepared by a simultaneous dispersing of surfactant and particles, so that the SMO molecules adsorb onto the nanoparticles' surface before any emulsion was produced. It was found that increasing concentration of silica has a weak influence on the emulsion properties and stability in terms of crystallization, but noticeably decreased the rate of emulsion crystallization in the presence of excess SMO. By contrast, the stability enhancement was even more pronounced at low SMO concentrations, when the particles start to dominate over the surfactant. The input of the combination of two types of relatively hydrophobic silica particles, one of which is surface-active and the other is not, is even more pronounced in terms of emulsion stability. The improved stability is related to the presence of one type of colloidal particles (surface-active) or their arrangements at the water/oil interface creating a "strong protective shell" for the droplets, whereas nanoparticles of another type (surface-inactive) remain in the oil phase providing a three-dimensional network among the shelled droplets and particles.

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