



# Emulsion behavior control and stability study through decorating silica nano-particle with dimethyldodecylamine oxide at n-heptane/water interface

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## HIGHLIGHTS

- Ludox silica nano-particles has a positive effect stabilizing emulsion. The synergism between SNPs and surfactant were studied by multiple methods with the concentration of surfactant as variable.
- Double phase inversion and its influence on emulsion stability were discussed.

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## ABSTRACT

Emulsions have been widely applied in subterranean enhanced oil recovery processes, cosmetics and chemistry engineering fields, etc. Current research interests are focusing on improving the stability of emulsion by involving surfactants or colloidal materials. This work aims to enhance the emulsion stabilization by introducing silica nanoparticles (SNP) surface-hydrophobized/hydrophilized by adding dimethyldodecylamine oxide (OA-12) and to reveal the dynamic behaviors of such composites on the liquid–liquid interface. The synergistic effect between SNPs and OA-12 in solution and on oil/water interface were studied by measuring the zeta potential, interfacial rheology and emulsion viscoelastic rheology, etc. It was found that the oil/water interface viscoelastic modulus are augmented by modified silica nano-particles and at the same time emulsions acquired significant long-time stability. Furthermore, phase transformation was induced with the increase of the concentration ratio between OA-12 and silica nano-particle, the emulsion type change from o/w, then to w/o and back to o/w. It is suggested that the inversions are induced by the mounting adsorption of OA-12 molecules on SNPs, which changes the hydrophilic-lipophilic balance of particle surfaces.

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## 1. Introduction

Colloid particles, including silica particles, applied for pickering emulsions stabilization have been studied extensively since its discovery in 1907 (Pickering, 1907). It has been applied massively in fields including oil recovery, cosmetics and food industries, etc. (Stuart et al., 2010; Wakefield and Park, 2007).

Recent studies of emulsions stabilized by mixtures of surfactant and nano-particles have focused on their behaviors and properties. Particles of alumina, silica, carbon or barium sulfate have been

researched as composites with various surfactants of cationic, anionic or polymeric (Gelot et al., 1984; Lagaly et al., 1999; Gosa and Uricanu, 2002; Legrand et al., 2005; Johansson et al., 1995).

The capability of these surfactant/particle composites on emulsion stabilization depends on the adsorption of surfactants on the particles surface and the particles on the oil/water interface (Mehta et al., 2015). Hassander et al. had studied the mechanism of oil-in-water emulsions stabilized by small silica (Ludox) particles with costabilizers to induce silica particle agglomeration, and proposed a popular stabilization mechanisms: silica particles agglomeration in bulk and adsorption at the oil/water interface (Hassander et al., 1989). Following this case, composite of cetyltrimethylammonium bromide with silica nano-particles/SNPs

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stabilized emulsions was studied by Binks and Rodrigues. In which, they proved the adsorption of surfactant on particle surface which leads to particle aggregation, and such aggregation had excellent adsorption ability on oil/water interface, which provided emulsions with standout long-term stability as a result (Binks and Rodrigues, 2007).

Lan et al. studied the influence of variable factors on the CTAB and silica nano-particles composite. The effects of salinity, pH, silica nano-particles and CTAB concentration on the stability of emulsions were investigated (Lan et al., 2007). Xu et al. have studied w/o emulsion that was stabilized by a nanoscale single chain “tadpole-like” polymer particles along with its double phase reaction application (Xu et al., 2014). Perino et al. analyzed the influence of fumed silica particles on water-in-crude oil emulsions with multiple methods including stability examinations, interfacial tension measurements, dilatational interfacial rheology tests, shear rheology tests, and Cryo-SEM analysis. It seems mechanisms of emulsion with particles stability were largely influenced according to the particle wettability (Perino et al., 2013). Yazhgur et al. investigated the adsorption film of silica nano-particles modified by CTAB at the air/water interface by dilatational surface rheology and optical investigations. Variable factors like the surface strain and surfactant concentration might cause the surface elasticity reaching an extremely high value when particles aggregate in the dispersions (Yazhgur et al., 2013).

Kundu et al. studied the rheological behavior of surfactant-stabilized oil-in-water emulsions. Factors including temperature, fraction of oil, pH and concentration of anionic surfactant were studied exclusively. Researchers found that oil-in-water emulsions exhibit typical shear thinning behavior and shear stress and shear rate could be well coordinated by the power law and other non-Newtonian fluid models. In one of their studies, Herschel-Bulkley model was applied for analysis of rheological data. The combined effect of volume fraction and temperature on viscosity of emulsions was described with proposed correlation (Kundu et al., 2015, 2017, 2013).

Phase inversion of Pickering emulsions were also reported in literatures. Schulman and Leja explained the linkage between tri-phase contact angle of oil-water-solid interfaces and the preferred emulsion type by studying SDS surface-modified BaSO<sub>4</sub> composite. Phase inversion was induced when BaSO<sub>4</sub> powder as hydrophilic coated particles was added into oleic acid w/o emulsions. Continuing adding of BaSO<sub>4</sub> as hydrophobic coated particles converted o/w emulsions to w/o type (Schulman and Leja, 1954). Tambe and Sharma demonstrated the inversion of emulsions stabilized by calcium carbonate particles that has been surface-modified by stearic acid (Tambe and Sharma, 1993).

Synergism between surfactants and silica particles has been researched with details and depth. Our purpose of this study is to propose a new composite of surfactant and particles, and take insight into phenomena that appeared. Through comparative studies, types and stability were investigated for emulsions stabilized by surfactant surface-modified SNPs or surfactant alone. Zeta potentials, dilatational interfacial rheology tests, rheology and viscoelastic measurements of emulsions were conducted. The aim of our study is to find and prove the adsorption of surfactant OA-12/dimethyldodecylamine oxide onto silica, and hence study the properties of such composite on oil/water surface. OA-12, dimethyldodecylamine oxide, is a pH sensitive cationic/nonionic surfactant. In this study, all experiments were carried out at pH = 6 ± 0.2, when silica nano-particles are mostly negatively charged and dimethyldodecylamine oxide is cationic at this point. It appears the electrostatic attraction between these two components caused adsorption of surfactant molecules on SNPs.

## 2. Experimental section

### 2.1. Materials

Ultrapure water with a resistance of 18.25 MΩ was collected from a reverse osmosis unit (ULUPURE, UPT-II-5T). Hydrochloric acid (Sinopharm Chemical Reagent Co., Ltd, China, 36%) and sodium hydroxide (XiLong Co., Ltd, 96%) were used to adjust pH. The cationic surfactant, dimethyldodecylamine oxide (OA-12), was a gift from Shanghai Jianhong Industry., Ltd., with a concentration of 30%wt. The oil phase was n-heptane (Sinopharm Chemical Reagent Co., Ltd, ≥98.5%). The silica nano-particles, LUDOX® HS-30 colloidal silica, was purchased from Sigma-Aldrich as a 30 wt% suspension with a pH of 9.8, surface area of 220 m<sup>2</sup>/g and density of 1.21 g/mL at 25 °C. The Ludox HS-30 silica nano-particle dispersion has an average size around 13 nm. The diameter measurement is depicted in Fig. 1.

### 2.2. Methods

#### 2.2.1. Preparation of aqueous dispersions and solutions

For OA-12-only solutions, OA-12 were diluted into target concentrations in 40 mL glass bottles. For OA-12 in nano-particles dispersions, first, the 30 wt% silica dispersion was diluted to 2 wt% aqueous dispersion with ultrapure water. Then, different portions of OA-12 was weighed into 40 mL glass bottles, then diluted by formerly prepared 2 wt% silica nano-particles aqueous dispersion. The concentration range of surfactant was from 0.014 mol·L<sup>-1</sup> to 6.568 mol·L<sup>-1</sup>. All dispersions were investigated at pH = 6 ± 0.2. The solutions or dispersions were stirred for ten minutes first and then the pH was lowered to 6 ± 0.2 by addition of HCl/NaOH dilution. Aggregation was measured by height and weight in the order of concentrations. A Malvern Zetasizer HS-3000 instrument was equipped for zeta potential measurements for OA-12 and SNPs composite dispersions. All measurements were repeated twice at least for valid results. Supernatant was taken for measurements for dispersions that have agglomeration. After the stability inspection of different concentrations of OA-12, some of these samples was selected for further investigation of interfacial rheology properties.

#### 2.2.2. Preparation and characterization of emulsions

Equal volumes of oil and water (10 cm<sup>3</sup> each) were prepared in 40 mL glass bottles. Emulsions were prepared with homogenizer with a stirring speed at 10,000 rpm for 4 min. Before homogenization, these dispersions were stabilized for 24 h after pH

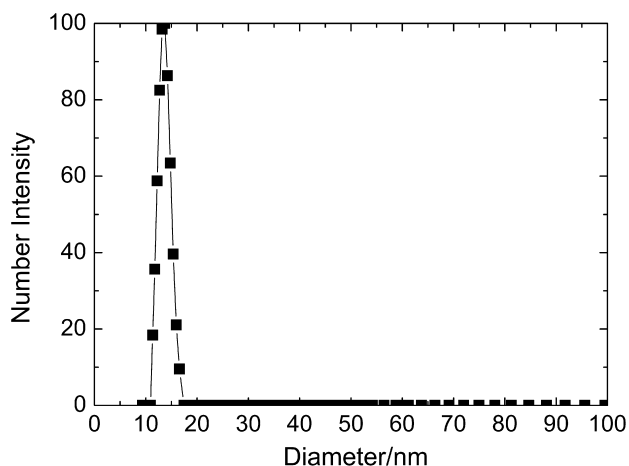


Fig. 1. Diameter distribution of Ludox HS-30 silica nano-particles at pH = 6 ± 0.2.

adjustment. Emulsion type was determined by dispersing into continuous phase. Emulsion volumes were recorded for evaluation of stability and coalescence degree. Microscopy investigation was carried out on a Leica DMI8 C inverted microscope system equipped with a Photron Fastcam SA-Z high speed camera. Photos were taken while a drop of emulsion diluted in its continuous phase was dropped nearby a cover slip on a microscope slide, and gently covered with another cover slip forming a wedge cavity containing the emulsion fluid. Image pro plus software was used to count/size the emulsion size distribution. Rheological measurements were performed using a coaxial cylinder sensor system equipped Haake RS6000 rheometer. The shear rate is from 0.01 to 100  $\text{s}^{-1}$  in steady shear measurements. When linear viscoelastic region was determined, frequency sweep measurements were conducted as a function of frequency.

### 2.2.3. Dynamic interfacial properties

Solutions of 0, 0.014, 0.058, 0.088, 0.177 and 0.144  $\text{mol}\cdot\text{L}^{-1}$  of OA-12 surfactant at  $\text{pH} = 6 \pm 0.2$  as control group and 0, 0.014, 0.058, 0.088, 0.177 and 0.144  $\text{mol}\cdot\text{L}^{-1}$  of OA-12 surfactant with 2 wt% SNPs dispersions at  $\text{pH} = 6 \pm 0.2$  as experimental group were prepared. Interfacial measurements were performed with a dynamic interfacial oscillatory drop tensiometer, Tracker-H, from Teclis France. The tensiometer was equipped with a CCD digital camera to record the drop profile in real time. The dynamic dilatational elasticity modulus and interfacial tension were recorded with time. The drop and bulk densities were 0.684  $\text{g}\cdot\text{cm}^{-3}$  and 1.02  $\text{g}\cdot\text{cm}^{-3}$ , respectively. To produce a rising drop of proper size, a U-shape needle of 1 mm inner diameter was applied. The method for interfacial rheology tests were area investigation by sinusoidal oscillations with a period of 10 s, and five active cycles and blank cycles both (Perino et al., 2013).

## 3. Results and discussion

### 3.1. Aqueous dispersions

Silica nano-particles are substantially negatively charged because of silanol SiOH dissociation at  $\text{pH} = 6 \pm 0.2$ . The Ludox SNPs present excellent stability and dispersibility at  $\text{pH} = 6$ . It is easy to deduce that the particle surfaces were originally hydrophilic.

The zeta potential of aqueous dispersions were conducted to study the adsorption process. Measurements were conducted as a function of OA-12 concentration. Results are given in Fig. 2.

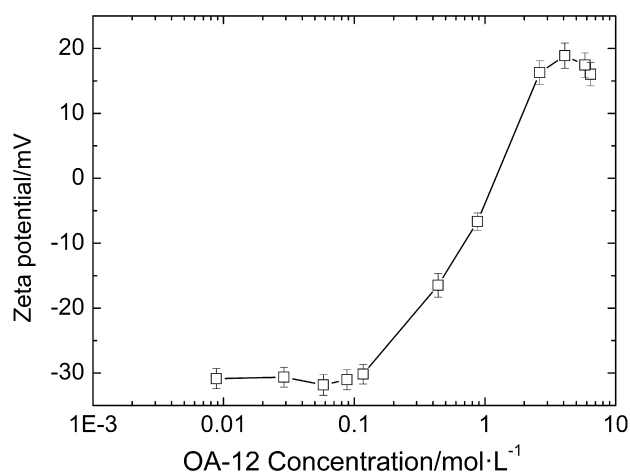


Fig. 2. Zeta potential of silica nano-particles in OA-12 solutions as a function of concentration.

The zeta potential of pure 2 wt% HS-30 silica nano-particles dispersion is  $-30$  mV at  $\text{pH} = 6 \pm 0.2$  (Fig. 2.). The magnitude of potential raised up until 0.1 wt% with the continuous addition of surfactant, and became positive at around 2.045  $\text{mol}\cdot\text{L}^{-1}$  indicating positively charged SNPs (Wang et al., 2004). This transformation tendency of zeta potential is well coordinated with the adsorption process of surfactant onto SNP surfaces.

Addition of cationic surfactant OA-12 results into electrostatic adsorption of surfactant monomers onto particle surface with surfactant tails pointing to bulk aqueous phase and heads clinging to particle surface. As more OA-12 molecules were attached to SNPs, particles exhibit increasingly hydrophobic property. When single-layer adsorption reached saturation, additional adsorption of surfactant can take place via chain-chain interaction between exposed surfactant hydrophobic tails on first layer and extra surfactant tails in the aqueous dispersion resulting in the formation of a di-layer. These di-layer surfactant had their head groups exposed to the aqueous phase. Hydrogen bond and electrostatic interaction between head groups and aqueous phase make the particles hydrophilic again (Fuerstenau and Jia, 2004). This progress is depicted in Fig. 3.

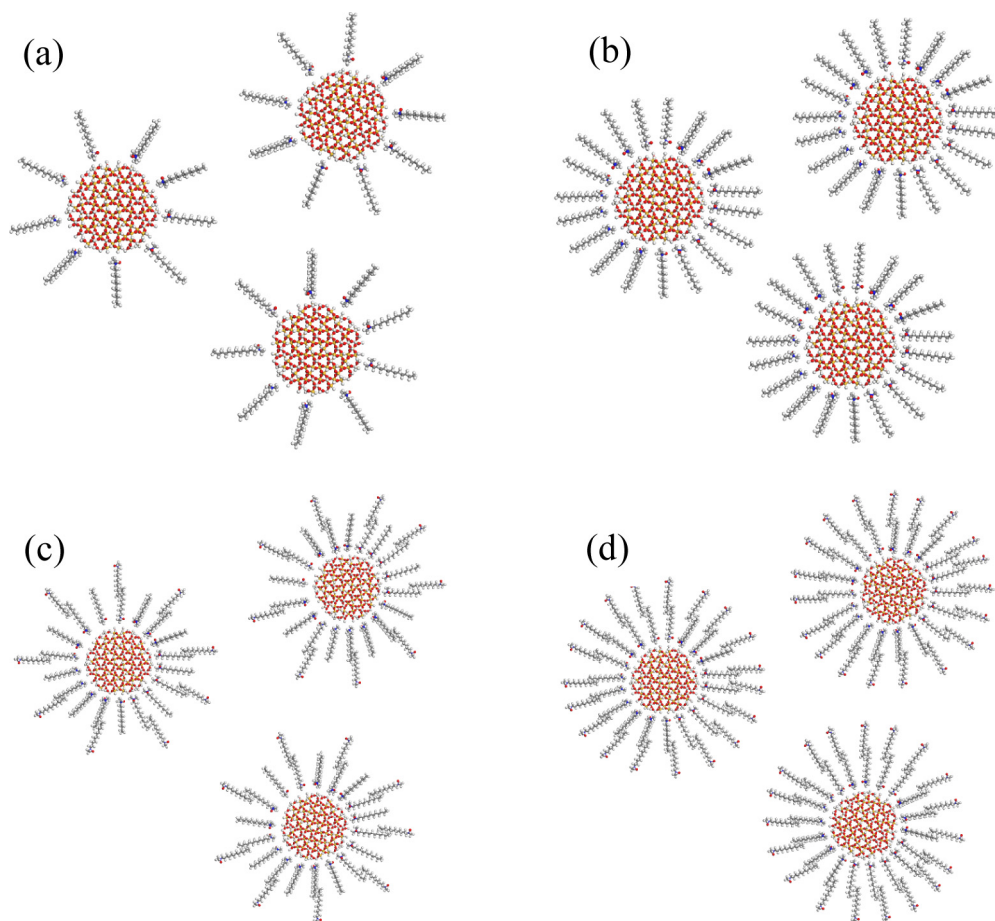
With constant silica nano-particles concentration at 2 wt%, aggregation appeared with continuous addition of OA-12 surfactant. The aggregation is complete within 12 h, and Fig. 4 shows the aggregation amount as a function of OA-12 concentration.

In Fig. 4, it can be seen that the stable dispersions were transparent and bluish below 0.582  $\text{mol}\cdot\text{L}^{-1}$ . With the increase of concentration of OA-12, the dispersions/solutions became turbid and the first peak of agglomeration volume occurred at 0.582  $\text{mol}\cdot\text{L}^{-1}$  OA-12. Subsequently, the aggregation volume decreased rapidly then leveled off at a relatively low level. Then the volume of aggregation rose up again starting at 2.627  $\text{mol}\cdot\text{L}^{-1}$  OA-12 and reached an maximum volume of 100% at 3.796  $\text{mol}\cdot\text{L}^{-1}$ . It should be reminded that at 3.503 and 3.796  $\text{mol}\cdot\text{L}^{-1}$  the aggregation present the viscous milk state with solid aggregation in the solution, which indicated the transition of solid agglomeration of silica nano-particles. Continuing addition of OA-12 made the dispersions transparent again. The neat agglomeration weight was also depicted in Fig. 4. The curve indicated a monotonic increase of SNPs agglomeration until 2.920  $\text{mol}\cdot\text{L}^{-1}$  with a subsequent decrease. The second summit value of agglomeration weight at 3.796  $\text{mol}\cdot\text{L}^{-1}$  is an example of total SNP weight contained in 10 mL dispersions.

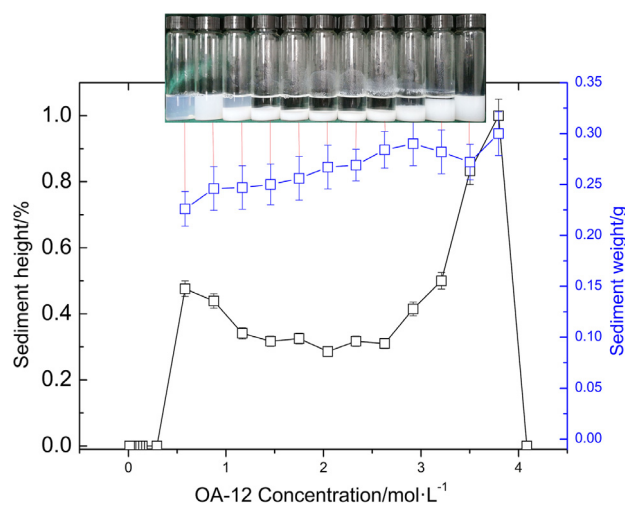
The aggregation height has two summits and the curve resembles a saddle, this is different to systems with CTAB-Nanoparticle (Binks and Rodrigues, 2007). Between zero and 0.144  $\text{mol}\cdot\text{L}^{-1}$  OA-12 while surfactant adsorption is modest, dispersions were stable and bluish, the surfactant monomers adsorbed onto the silica particles are not sufficient to reverse the bulk hydrophilic-lipophilic property, and the repulsion between particles dominates. The zeta potential values were also below zero.

Between concentrations of 0.582 and 2.045  $\text{mol}\cdot\text{L}^{-1}$  OA-12, progressively flocculation of particles was caused by strong van der Waals attraction between nearby alkyl chains of surfactants on neighboring particle. And this progress happened swiftly and the neat amount of silica nano-particles was increasing. The zeta potential at this phase increased, which indicated a change of surface charge of SNPs.

At concentrations between 2.045 and 3.503  $\text{mol}\cdot\text{L}^{-1}$ , the particles are mostly hydrophobic and the pile of particles aggregation becomes intense. The aggregation is made up of solid particles formed network structure, which enhanced the density of this phase. At high surfactant concentrations, the close contact between micelles and particles might have cause such flocculation (Furusawa et al., 2002). After a period of growth, above 3.796  $\text{mol}\cdot\text{L}^{-1}$  OA-12, the formation of surfactant di-layer on silica nano-particles is near implemented and the particles have been



**Fig. 3.** Adsorption of surfactant monomers onto SNPs. (a) describes a low concentration of OA-12 in the SNPs dispersions when SNPs were only partially covered by surfactants; (b) describes a mediate adsorption of surfactant onto SNPs forming full monolayers; (c) describes a higher OA-12 concentration with bilayers formation in progress; (d) describes SNPs with bilayers in dispersions with very high OA-12 concentrations. The cores in the middle of each composite are SNPs, and the surrounding molecules are surfactant OA-12 molecules. The sizes in this figure are not the actual sizes.



**Fig. 4.** Aggregation heights and weights of mixture of silica nano-particles and OA-12 as a function of OA-12 concentration and corresponding images of dispersions. Concentrations are 0.144, 0.293, 0.582, 0.876, 1.169, 1.458, 2.627, 2.920, 3.209, 3.503, 3.796 mol/L, respectively.

fully converted into hydrophilic particles. The dispersions turned transparent and bluish again with continuing increase of OA-12 concentration.

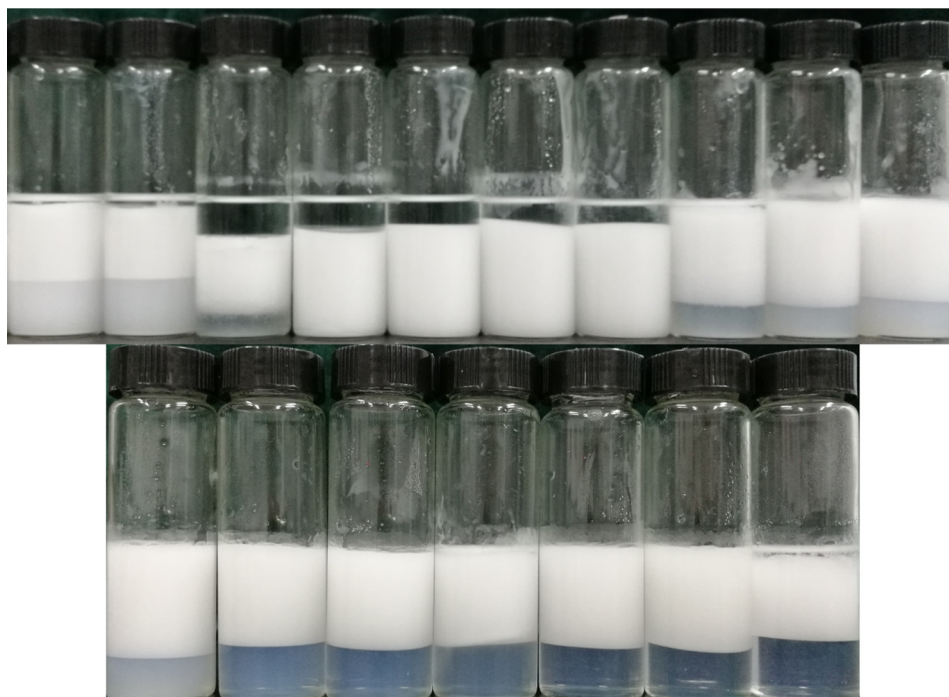
### 3.2. Emulsions stabilized by surface-modified SNPs and surfactant alone

#### 3.2.1. Double phase inversion

The picture of emulsions prepared from aqueous dispersions of SNPs (2 wt%) and increasing OA-12 concentration 24 h after preparation is shown in Fig. 5.

The wettability of OA-12 modified SNPs depends on the OA-12 concentration in dispersions. Hydrophilic particles tend to stabilize o/w emulsions, and w/o emulsions favors hydrophobic particles (Fuerstenau and Jia, 2004). When the OA-12 concentration is lower than  $1.169 \text{ mol}\cdot\text{L}^{-1}$ , the emulsion type is o/w, the same as OA-12-only emulsions (Fig. 6). As the concentration continues to increase, the emulsion phase inversion is induced into w/o type, then inter-phase and o/w again. This inversion progress critically depends on the concentration of the surfactants.

At low concentrations between  $0.014$  and  $1.169 \text{ mol}\cdot\text{L}^{-1}$ , the surfactant monomers adsorbed onto the silica particles form a partially mono-layer with their hydrophilic heads facing the particle surface and hydrophobic tails heading towards the aqueous phase. The aqueous phase of this range of concentration is still hydrophilic and tends to induce o/w emulsions, which is well corresponding to experimental results. As depicted in last section, the mono-layer on silica particles only becomes complete when the concentration of OA-12 reaches around  $2.045 \text{ mol}\cdot\text{L}^{-1}$  when the agglomeration is most stabilized. The emulsion experiments also show that between  $1.458$  and  $2.334 \text{ mol}\cdot\text{L}^{-1}$ , the silica particles are mainly



**Fig. 5.** OA-12 and silica nano-particles composite stabilized emulsions with a concentration range from 0.014 to 3.209 mol·L<sup>-1</sup>. The concentration decreases from left to right and up to bottom.



**Fig. 6.** OA-12-only emulsions with a concentration range from 0.014 to 4.378 mol·L<sup>-1</sup>. The concentration decreases from left to right and up to bottom.

hydrophobic. When the concentration is between 2.627 and 3.209 mol·L<sup>-1</sup>, the emulsions are of o/w type. At 3.209 mol·L<sup>-1</sup>, the formation of di-layer of surfactant on silica particles is probably completed and the particles become hydrophilic to a maximum extent. This is well coordinated with the theory of double layer forming of surfactant adsorbing onto silica particles and data analysis of aggregation of mixed silica particles and OA-12 solutions.

### 3.2.2. Microscopy and static observation of emulsions

By microscopy inspections, the influence of nano-particles on the droplet sizes were observed and is shown in Fig. 7. Microscopy pictures were taken to prove the changes of droplet sizes, as shown in Figs. 8 and 9. These images and data of droplets and their sizes were recorded 27 days after emulsion preparation (see Fig. 10).

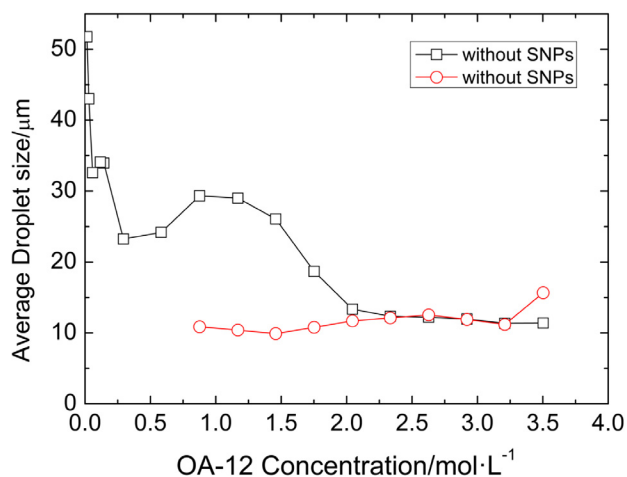


Fig. 7. Droplet size evolution of emulsions as a function of concentration.

It can be seen that the droplet sizes of OA-12 with SNPs o/w emulsions were similar to those of OA-12-only o/w emulsions at higher concentrations, generally speaking. Droplet sizes are obviously related to the adsorption of SNPs on the oil/water interface, but also have taken influence from aggregations of SNPs. For emulsions with SNPs, o/w emulsion drops formed at low OA-12 concentrations (below  $1.169 \text{ mol}\cdot\text{L}^{-1}$ ) are two to four times larger than w/o emulsion drops formed at higher OA-12 concentrations (above  $1.169 \text{ mol}\cdot\text{L}^{-1}$ ). The deformation also happens with o/w emulsion drops, which should be ascribed to the thin membrane formed by the adsorption of SNPs on the oil/water interface.

From Fig. 7, with the decrease of hydrophilicity comes decreasing sizes of emulsion drops and forming of single layer of surfactants on SNPs. The first turn of droplet sizes curve corresponds with the increase of hydrophilicity and formation of second layer of surfactants on SNPs. This evolution of emulsion droplet sizes is a reinforcing evidence of the double layer on SNPs theory and

evolution of hydrophilicity/hydrophobicity of aqueous dispersions of SNPs.

### 3.2.3. Static stability and synergism observation

In order to understand the improvement of stability by adding of silica nano-particles, The preferred emulsions with n-heptane in a system containing OA-12 alone as control group and another containing OA-12 and SNPs as treatment group were investigated.

At  $\text{pH} = 6 \pm 0.2$ , Ludox HS-30 particles are poor emulsifiers (Binks and Rodrigues, 2007). This fact reminds us that raw silica nanoparticles are very hydrophilic and negatively charged, and their adsorption to the oil/water interface is unstable (Binks and Horozov, 2006). On the contrary, OA-12 reveals itself as a good emulsifier when its concentration is sufficiently high. The emulsion type with OA-12 alone are all in all o/w, as shown in Fig. 6. The stability of OA-12-only emulsions is also considerable at some concentrations, relatively speaking, as shown in Fig. 11.

The emulsification ability of OA-12 is also remarkable and steady. Above  $0.876 \text{ mol}\cdot\text{L}^{-1}$  OA-12, the control group emulsions volumes stopped increasing. A few emulsions stood for three-weeks of high concentrations are still maintaining their status as stable as two weeks ago.

For OA-12-only emulsions, the increase of stability is owing to the increase of the surfactant adsorption on the interface of oil/water. The oil drops surrounded by surfactant mono-layers isolated each other and forged barricades to stop coalescence process. Once the adsorption is complete, the emulsification volumes of these emulsion systems were settled. Between  $0.582$  and  $1.169 \text{ mol}\cdot\text{L}^{-1}$ , the increase of concentration of OA-12 below cmc enhanced the stability of emulsions dramatically. The surfactant monomers adsorbed onto the interfaces and formed a mono-layer to stabilize the oil/water interface. Above  $2.334 \text{ mol}\cdot\text{L}^{-1}$ , the increase of micelles in aqueous solutions is the main factor that affect the stability of emulsions.

Many researches have reported the stability enhancement ability of nano-particles on emulsion systems (Cui et al., 2008; Worthen et al., 2014). The emulsion creaming degree of OA-12

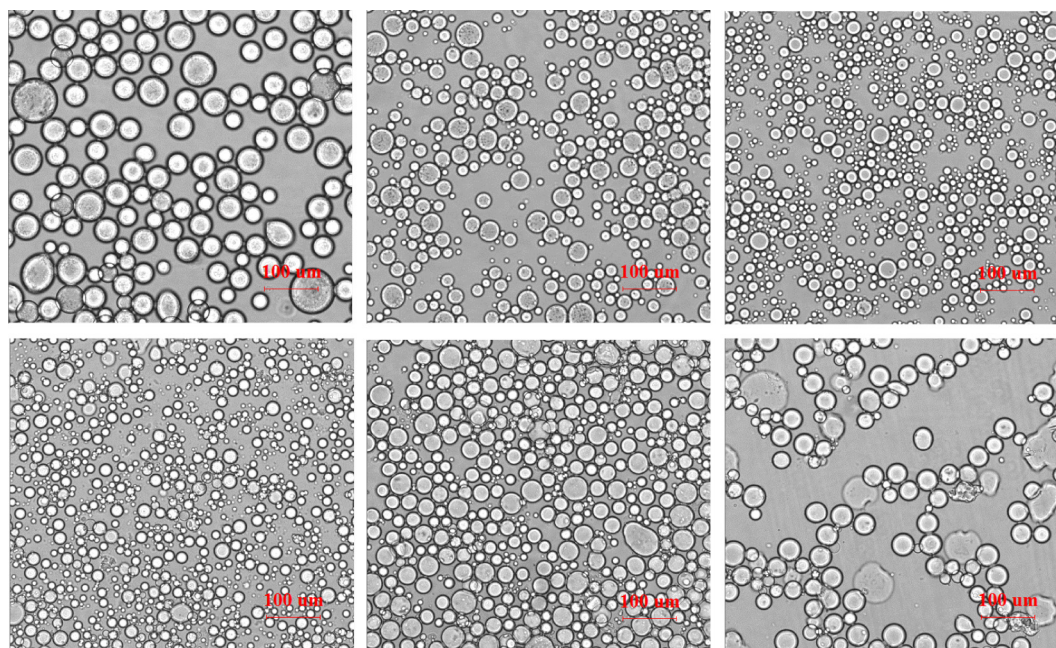
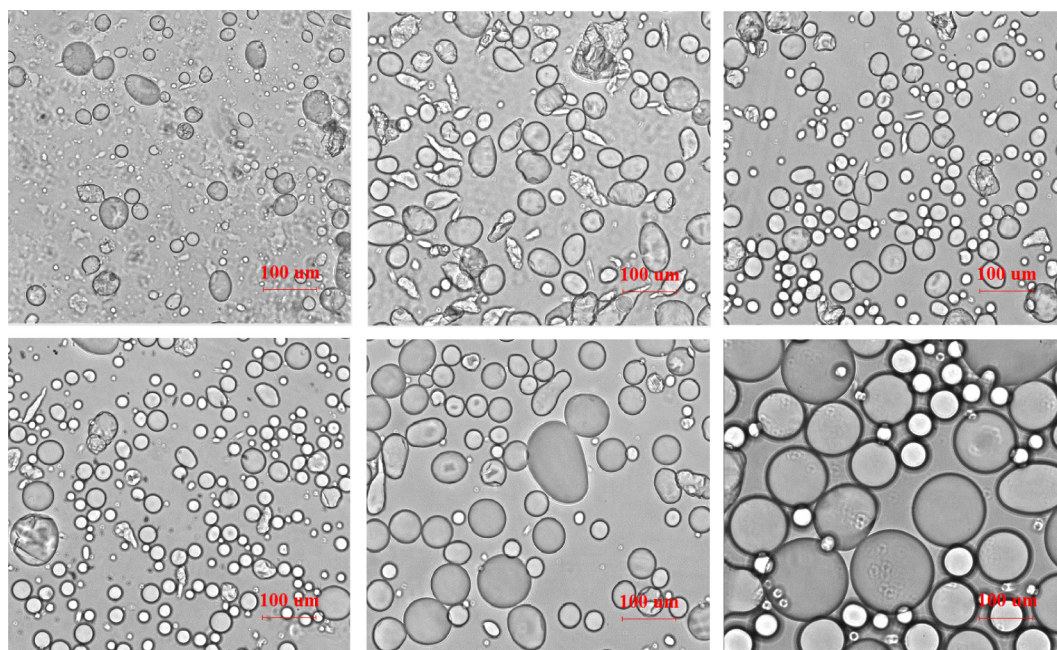
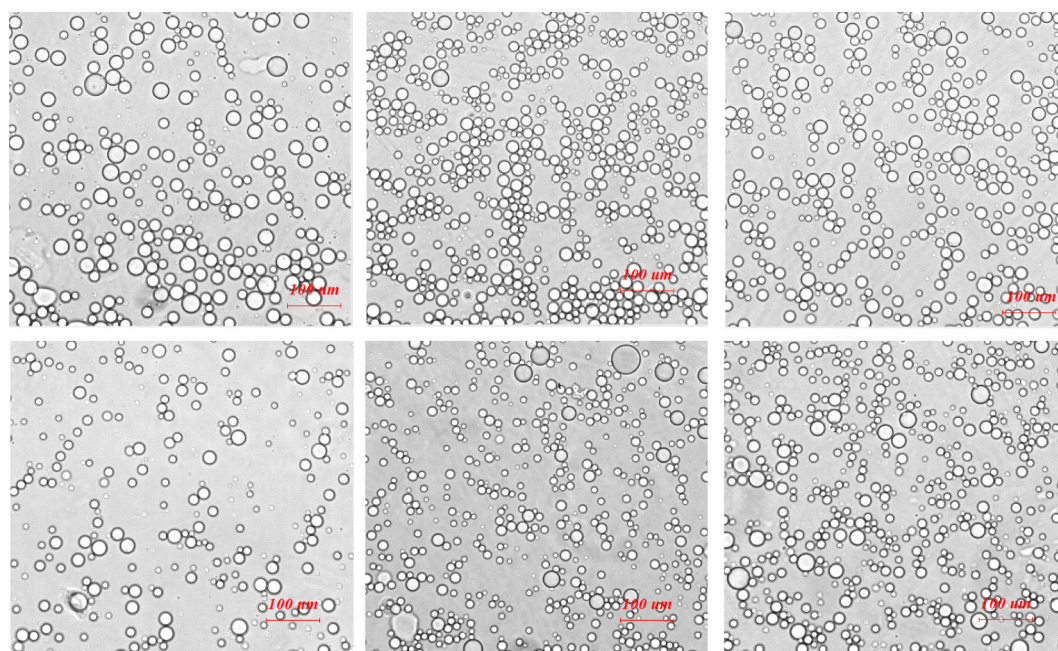


Fig. 8. Optical microscopy images of w/o (water-in-oil) emulsions of OA-12 with silica nano-particles. The concentrations of OA-12 are as follows: 4.085, 3.503, 2.334, 2.045, 1.751, and  $1.458 \text{ mol}\cdot\text{L}^{-1}$ .



**Fig. 9.** Optical microscopy images of o/w (oil-in-water) emulsions of OA-12 with silica nano-particles. The concentrations of OA-12 are as follows: 2.920, 1.169, 0.876, 0.293, 0.088, and 0.014 mol·L<sup>-1</sup>.



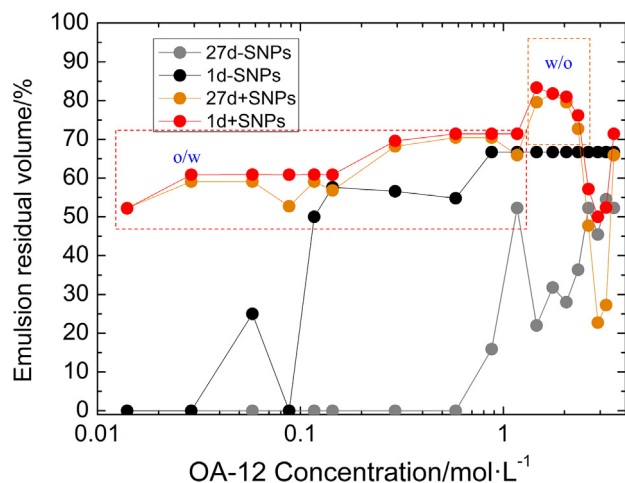
**Fig. 10.** Optical microscopy images of OA-12-only emulsions (oil-in-water emulsions). The concentrations of OA-12 are as follows: 4.085, 3.503, 2.920, 2.334, 1.751, and 1.169 mol·L<sup>-1</sup>.

emulsions with silica nano-particles were also recorded and depicted in Fig. 11. It is easy to be seen that synergism between SNPs and OA-12 helped to enhance the stability of emulsions, since emulsions stabilized by composite of OA-12 and SNPs were far more stable than those of surfactant only at respective concentrations.

Below 2.334 mol·L<sup>-1</sup>, which should be reminded as the second phase inversion point when the emulsions turned from o/w into w/o type, the stability and emulsification ability of OA-12 with particles are both superior than OA-12-only emulsions. After 27 days,

the emulsions stabilized by OA-12 -SNPs only lost a slight volume compared to the gravely volume reduction of OA-12-only emulsions.

Agglomerations appeared when the solutions of mixed nano-particles and surfactant at pH = 6 ± 0.2 were prepared. Earlier studies reported this phenomenon and explained the correlation between amount of flocculation and emulsion stability (Binks and Rodrigues, 2007). The adding of silica nano-particles should be the cause of stability reformation of emulsions. At lower concentrations below 0.582 mol·L<sup>-1</sup> OA-12, the stability reformation



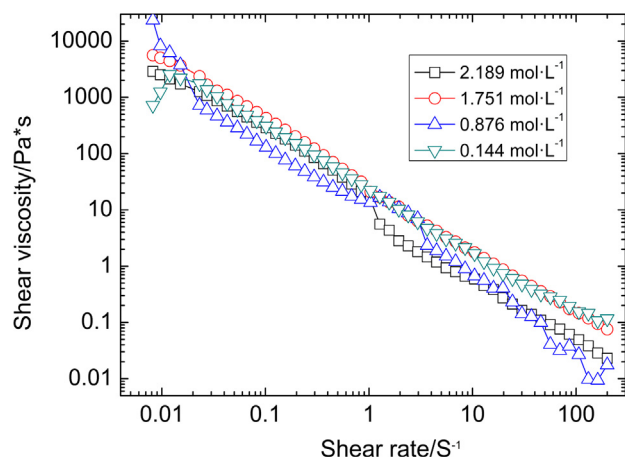
**Fig. 11.** Emulsion residual volume of systems with (27d + SNPs and 1d + SNPs) or without (27d-SNPs and 1d-SNPs) silica nano-particles of one day and 27 days as a function of OA-12 concentration. The type of emulsions were marked as o/w (oil-in-water), or w/o (water-in-oil).

mostly depends on the adsorption of silica nano-particles onto the oil/water interface. Between 0.582 and 3.209 mol·L<sup>-1</sup>, the emulsions coalescence is inhibited by coagulation and agglomeration of silica particles.

The agglomeration formed by silica nano-particles and the silica nano-particles adsorbed on the oil/water interface strengthened the interface. These agglomerations or silica nano-particles are either formed and deposited when preparing the OA-12 solutions with nano-particles or dispersed in the OA-12 solutions and stalled the coalescence and breaking of emulsions. As shown in Fig. 5, the emulsification of OA-12 with silica nano-particles increased along with the adding of OA-12. And a sudden jump of emulsion volume is detected when the phase inversion happened at 1.458 mol·L<sup>-1</sup> concentration of OA-12.

#### 3.2.4. Dynamic stability and synergism observation

The steady shear and oscillatory measurements were conducted on emulsions with OA-12 concentrations of 0.131, 0.876, 1.751 and 2.189 mol·L<sup>-1</sup> and SNPs of 2 wt%. Measurements of control group of OA-12-only emulsions were also carried out, but the emulsions were highly unstable when exposed to the shear stress and thus no valuable data were recorded. The viscosities of emulsions with different shear rates are shown in Fig. 12.



**Fig. 12.** Shear viscosities of emulsions stabilized by silica nano-particles at varied concentrations as a function of shear rate.

It is easy to conclude that the viscosities of emulsions vary according to different concentrations of surfactant and decrease with increasing shear rates, exhibiting a typical shear thinning behavior. This phenomenon of viscosity reduction could be ascribed to the breaking of emulsions, meaning the emulsions could be vulnerable when exposed to shear stress.

Ostwald-de Waele (power law) model:

$$\eta = K\dot{\gamma}^{n-1} \quad (1)$$

Under different concentrations, the shear thinning behavior of four emulsions follow the same pattern. To evaluate them mathematically, Ostwald-de Waele (power law) model was applied to simulate the non-Newtonian behavior of emulsions. Ostwald-de Waele (power law) model (Eq. (1)) is frequently used for non-Newtonian fluids, including emulsions, to describe the time-independent steady shear phenomenon. There are two parameters in the power law model: flow consistency index  $K$  and flow behavior index  $n$  (see Table 1).

From power law model analysis, higher flow consistency index  $K$  usually means higher viscosity, so  $\eta_{1.751} > \eta_{0.144} > \eta_{2.189} > \eta_{0.876}$ . The absolute  $n$  values indicate the emulsions are pseudoplastic fluid, which is typical fluid type of emulsions (Kundu et al., 2017).

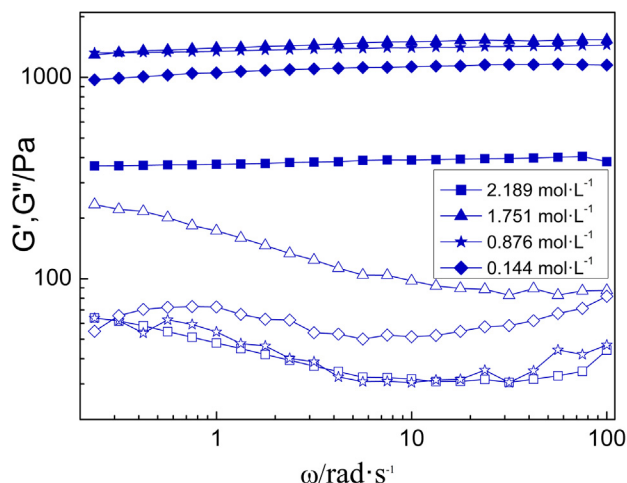
Oscillatory measurements were also conducted to investigate viscoelastic properties of emulsions of the concentrations of 0.131, 0.876, 1.751 and 2.189 mol·L<sup>-1</sup> OA-12 with 2 wt% silica nano-particles. The storage modulus ( $G'$ ) and loss modulus ( $G''$ ) versus frequency ( $\omega$ ) at a fixed shear stress ( $\sigma = 1$  Pa) were recorded and shown in Fig. 13. The loss modulus  $G''$  has different trends with different concentrations. At higher concentrations like 1.751 mol·L<sup>-1</sup>, there is a mild slope with the increase of frequency until reaching a minimum and then a slight increase.

Unlike viscoelastic rheological properties of surfactant micelles (Zhao et al., 2015), the modulus  $G'$  and  $G''$  have no intersection point in this case. The fact that  $G'$  is larger than  $G''$  indicated a gel-like elastic rheological behavior. The weak dependency of

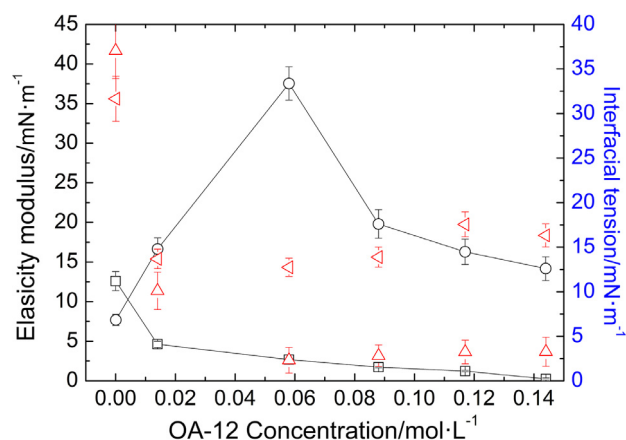
**Table 1**

Flow parameters determined by the Ostwald-de Waele (power law) model.

| Concentration/(mol·L <sup>-1</sup> ) | $K$ (Pa·s <sup><math>n</math></sup> ) | $n$    | $R^2$  |
|--------------------------------------|---------------------------------------|--------|--------|
| 2.189                                | 12.307                                | -0.34  | 0.9916 |
| 1.751                                | 27.369                                | -0.147 | 0.9988 |
| 0.876                                | 11.483                                | -0.274 | 0.9822 |
| 0.144                                | 21.718                                | -0.062 | 0.99   |



**Fig. 13.** The storage modulus ( $G'$ ) and loss modulus ( $G''$ ) versus frequency ( $\omega$ ) at a fixed shear stress ( $\sigma = 1$  Pa) of different concentrations.



**Fig. 14.** Dynamic elasticity moduli and interfacial tensions of two groups as a function of OA-12 concentration. “○”, “□”, “△”, “▽” represent elasticity moduli of OA-12 with SNPs, OA-12 solutions, interfacial tension of OA-12 with SNPs and OA-12 solutions, respectively.

moduli upon frequency also indicated the emulsions' highly elastic structure (Chevalier and Bolzinger, 2013). The increased gel strength at higher OA-12 concentration where emulsion volumes varied slightly was mostly due to the reduction of emulsion droplet size (as proved by the microscopy images and measurements), thus a more dense arrange of oil droplets. And different types of emulsions should be inspected separately. At 2.189 and 1.751 mol·L<sup>-1</sup> of OA-12, the emulsions are w/o and the emulsions are o/w at 0.876 and 0.131 mol·L<sup>-1</sup> concentration. Although the droplet sizes show a linear decrease trend, the emulsion type is another fatal factor affecting the viscoelastic rheology properties. Apparent viscosities of nano-particles stabilized emulsions decreased as the shear rate increased (Fig. 12).

The adsorption of SNPs on the interface forged a dense solid layer as a physical barrier between nearby emulsion droplets, which diminished the possibility of coalescence. This concept has been recognized as a main reason for stability enhancement of emulsion systems (Xiao et al., 2016).

### 3.2.5. Interfacial property of surfactant and silica nano-particles composite on oil/water interface

The dynamic surface tension and dynamic dilatational surface elasticity measurements were conducted at 0, 0.014, 0.058, 0.088, 0.117 and 0.144 mol·L<sup>-1</sup> OA-12 with fixed HS-30 silica nano-particles concentration at 2 wt%. A series of OA-12-only solutions were prepared as control group and another series of OA-12 with HS-30 silica nano-particles dispersions were prepared as treatment group. The surface tensions and elasticity moduli were recorded and shown in Fig. 14. Above this range the OA-12 solutions with silica nano-particles were turbid or silica nano-particles settled into agglomeration, and thus they are inappropriate for interfacial measurements.

Since the emulsions at these concentrations are all o/w, the rising drop method has been used to determine the viscoelasticity of the interface with OA-12 solutions or mixtures of OA-12 and silica nano-particles as bulk phase and n-heptane as drop phase (Ravera et al., 2006; Whitby et al., 2012; Ravera et al., 2008).

Based on the analysis in the last section, silica nano-particles modified by surfactants exhibit hydrophilic properties (OA-12 concentration below 0.144 mol·L<sup>-1</sup>), because the adsorption mono-layer of surfactants on particles is only partly complete. The addition of OA-12 increased the hydrophobic property of the particles with increasing adsorption. The SNPs/surfactant composite adsorbing on the oil/water interface raised the surface tension

by four to six times compared to surfactant only systems, as seen in Fig. 14. With the increase of surfactant concentration, both curves of interfacial tension follow the same trend with a steep descent and steady plateau. The participation of surfactant has significantly decreased interfacial tension. However, the involvement of SNPs increased it. This phenomenon could be ascribed to the selective adsorption of surfactants on oil/water interface and SNPs surfaces when the electrostatic force between SNPs and surfactants stole surfactant molecules away from oil/water interface.

The addition of silica nano-particles also enhanced the elasticity moduli of the oil/water interface. This explained the stability reformation at low OA-12 concentrations when there is no agglomeration forming. The unsaturated adsorption of surfactants onto the particles formed numerous half hydrophilic and half hydrophobic composites. These composites spontaneously assemble on the oil/water interface with their hydrophilic half facing the water phase and hydrophobic half facing the oil phase. These composites are also highly stable since the only contributory factor is the concentration of OA-12 monomers.

## 4. Conclusion

Focusing on the stability performance and synergism mechanism of emulsions with the addition of Ludox silica nano-particles and the concentration increase of OA-12, a cationic surfactant, we studied the influence of silica nano-particles on the OA-12 emulsions and the interfacial properties of oil/water interface.

Without silica nano-particles, the OA-12 emulsions are all o/w type and of poor stability. The adding of silica nano-particles not only enhanced the long-term stability and emulsifying capacity of the emulsions in a certain range, but also induced a double phase inversion.

Rheology properties, surface tension and dynamic dilatational surface elasticity measurements proved the viscoelasticity and interface strengthen ability of the layered silica nano-particles. The phase inversion is induced by the adsorption of increasing amount of surfactant onto the silica nano-particles from mono-layer to di-layer. Through aggregation study and zeta potential measurements of dispersions, and microscopy inspection (ie. droplet size determination) on emulsions, the transformation of the adsorption layer structure was proposed.

At low surfactant concentrations, the enhancement of stability of emulsions with SNPs were due to the adsorption of SNPs onto the oil/water interface. For higher surfactant concentrations, the solid materials in emulsions like agglomeration formed by silica nano-particles and the silica nano-particles adsorbed on the oil/water interface strengthened the interface. It is clear that the agglomeration of SNPs is of better effect for emulsion stability.

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## Competing interests statement

The authors declare that they have no competing interests.

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