



Aqueous Foams Stabilized by Hydrophilic Silica Nanoparticles via In-Situ Physisorption of Nonionic TX100 Surfactant

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(Received: November 29, 2012; Accepted in Revised Form: February 4, 2013)

Abstract: This paper present the study of aqueous CO₂ foam prepared by a mixtures hydrophilic silica nanoparticles and non-ionic Triton X100, TX100, surfactant. The synergistic effects of the mixture on stabilizing the CO₂ foam were inferred into few key parameters namely; particles and surfactant concentration, adsorption of surfactant onto the particles via surface tension and adsorption isotherm, foam lifetime and, the size of the bubbles produced. It was found that the adsorption behaviour of TX100 on silica surface exhibit a particular characteristics depend on the concentration of silica, high total surface area available leads to high adsorption of surfactant molecules. The synergetic performance of silica/TX100 in stabilizing foam can be observed at low (0.01%) and intermediate (0.1%) concentration of TX100. Lower concentration required low silica concentration while the intermediate concentration required high silica fraction in the dispersion to stabilize the foam.

Key words: Adsorption • Silica nanoparticles • TX100 • Foam stability

INTRODUCTION

Having used in wide range of application such as foods, personal care products and even in industrial process such as cleaning, pharmaceutical, floatation, water treatment and enhanced oil recovery, foams stability become an important factors in the area involved [1-3]. Surfactant used in stabilizing the foam were found to be ineffective for large scale application such as enhanced oil recovery as they tend to degrade before they fulfil their duty [4]. Particles can act in similar way as surfactant [5] with factor governing the stability are mainly relies on particles size, shape, concentration and their hydrophobicity [6-7].

Foam stabilized via utilizing the nanoparticle materials have become the topic of interest among researchers these past few years [8-14] although the early studies on this area was already being conducted back in late 80's [15] and later on in the study of food in 2004 [16]. The result from previous studies shows that the stability of foam stabilized by particles was highly dependable on the degree of hydrophobicity [8, 11-13, 15, 17-21] of the particles which is inherently hydrophilic in their nature [17-18]. As the hydrophobicity of the particles becomes the main factor for stabilization mechanism mainly because of their firm attachment on the gas-liquid

(air-water) interfaces [5-6], a sufficient concentration of nanoparticles was viewed as an influenced parameter rising from their saturation inside the thinning film that will further slowing down the liquid drainage by forming steric barrier against coalescence [6, 9].

Due to economic consideration, rendering the hydrophilic particles to partially hydrophobic can boost the production cost and thus the in-situ physisorption has become a preferable alternative to modify the surface properties of these particles [18, 22-23]. Zhang *et al.* [20] studied the combine effect of hydrophilic Laponite nanoparticles with non-ionic tetraethylene glycol monododecyl ether, C₁₂E₄, surfactant in stabilizing aqueous foam and conclusively found the enhancement in foam stability as the surfactant concentration increased. Some researchers used different type of particle for the same purpose [17, 19, 24] while some other used in the stability of emulsion study [25-27].

The study presented here will highlight on the carbon dioxide, CO₂, foam stabilized by hydrophilic silica, SiO₂ nanoparticles in the presence of non-ionic TX100 surfactant as our forward aim was to study this effect for enhanced oil recovery purposes via CO₂ foam flooding [10]. The effect of particles and surfactant concentration were studied thoroughly.

MATERIALS AND METHODS

Materials: Silica nanoparticles of 60-70 nm sizes were purchased from Nanoparticles Inc. with purity of 98% was received as white powder. Image analysis from SEM however shows that the size of the particles are slightly bigger than that of the given by the manufacturer, that is 70-90 nm. No modifications were made on the particles and it is used as it is received. With density of 2.17-2.66 g/cm³, these particles are insoluble in water. Triton X100 was supplied by Scharlau Chemie S.A in 1 liter bottle with a purity of more than 98%. Sodium chloride, NaCl from Molekula brand was used as to compensate for the free ions presence in the solution. CO₂ gases used in this study were obtained from Mega Mount Industrial Gases Sdn. Bhd. Since the gases used are for the industrial usage, the maximum purity of the gases was at 96%.

Method

Preparation of SiO₂-TX100 Aqueous Dispersion: Known mass of silica nanoparticles being tested at concentration of 0.1, 0.5, 1, 5 and 7wt% were first being dispersed into deionized water of known volume by using FAVORIT stirring hot plate at room temperature. The dispersions were then sealed and kept at room temperature for a week before use. Stock TX100 solution of concentration ranging from 0.01, 0.1, 0.5 and 1% were also being prepared. With proper ratio and dilution of stock dispersion prepared earlier, silica-TX100 dispersions were then being prepared and the dispersions were continuously stirred for another 12 hour to attain adsorption equilibrium. All experiments were carried out at their environment pH without any adjustment.

Viscosity of Silica-TX100 Dispersion: Viscosity of dispersion containing silica at concentration of 0.1 to 7wt% at various surfactant concentrations were measured by using Anton-Paar Rheometer at control temperature of 25-28°C.

TX100 Adsorption on Silica Nanoparticles: Adsorption of TX100 surfactant on silica nanoparticles via the so-call physisorption were measured by using two different methods. The first approach were determined by measuring the surface tension of the air-surfactant solution interfaces both with and without the presence of silica nanoparticles by using Kruss Tensiometer apparatus with a du Noüy Ring method and appropriate correction factor [26, 28]. Platinum-iridium ring used were rinsed and cleaned thoroughly for every sample being measured by using acetone and hexane as in the procedures described elsewhere [29]. The loss of

surfactant molecules as it is being adsorbed onto the silica particles were indicated by the increment in surface tension.

Adsorption isotherm of TX100 on silica was also being measured via UV depletion method. Dispersions were centrifuged at 15,000 rpm for 20 minutes as to separate the particles from supernatant [21]. The supernatants were then analyzed by using Buck Scientific 105 UV-Vis Spectrophotometer at 290 nm centred peak of TX100 solution in 10 mm path length cuvette.

Foamability and Foam Stability of Dispersions: Foams were generated by blending the 100 ml dispersions using laboratory blender at 14,000 rpm for 2 minutes as being described previously [30]. Instead of using blender jar, a transparent acrylic column of 7 cm diameter x 44 cm height was installed for better measurement. As to create the proper environment specifically for aqueous-CO₂ foams, a very slow flowrate of CO₂ gases were introduced at the bottom of the column and the gases were injected before and during blending the dispersion. Immediately after the blender was stopped, the foam and liquid volume was recorded and the observation was continued.

Stability of foam was viewed as normalized foam heights which have been calculated base on the changes of foam height as a function of time. Normalized foam height can be calculated by [20]:

$$\text{Normalized foam height} = \frac{\text{foam height (t)}}{\text{foam height (t=0)}} \quad (1)$$

where t is time in minute.

Image Analysis: The morphology of the bubbles in term of shape and size distribution were analyzed by using Leica EZ4 HD Stereo Microscope integrated with 3 megapixel CMOS camera supplied by HistoCenter (M) Sdn. Bhd.

Particle Partitioning: T25 Basic IKA LABORTECHNIK homogenizer at a speed of same as the blender was used with a purge of CO₂ gases being introduced in the 50 ml beaker containing dispersion as to simulate the CO₂ environment. Particles attachment on the bubbles was quantified approximately as a function of TX100 concentration. For this measurement, settling time of 30 minute was used as indicator. Upon 30 minutes time is over after the foam preparation, syringe was used to suck out liquid drained containing silica nanoparticles from the foam and dried at temperature of 105°C.

The fractions of particles, x, attached on the air-water interface of the foam were then calculated by using;

$$x = \frac{(w_0 - w)}{w_0} \times 100\% \quad (2)$$

where w_0 and w represent the mass of dried silica nanoparticles upon the dispersion preparation and after drained from the foam, respectively.

RESULTS AND DISCUSSION

Properties of Silica-TX100 Aqueous Dispersion:

The behaviour dispersion of silica in TX100 solution was observed for 1 week. Figure 1 shows silica nanoparticles in 0.1% TX100 solution. pH of dispersion were tested at their environmental condition without any modification and found to be in the range of 6.47 to 6.90 with a little varies from one another. At lower particles concentration, dispersion happened to be cloudy. This behaviour indicates the movements of particles by which the suspension was said to be stable in turbid conditions [20]. Particles flocculation and phase separation, sedimentation became more obvious at high particles concentration. As been reported earlier [31], the flocculation may take place upon the addition of surfactant which then further said to form surface micelles. Viscosities of dispersion increase with the increase of particles concentration by substantial different from one another with the increasing in TX100 concentration.

Surface Tension: Surface tension of the equilibrium silica-TX100 dispersion was shown in Figure 3. In discussing the behaviour of colloidal system in the presence of surfactant, be it ionic or non-ionic, researchers found the interaction of surfactant monomers and the particles occurs within the bulk of the dispersion itself [11, 17-23, 25-27, 32-33] and thus the changes in surface tension of colloidal system were generally influenced by the added amount of whether surfactant or particle fractions. As being stated earlier [15], the changes in surfaces tension indicates the increment of hydrophobicity of the particles. The plotted graph clearly shows the gradual increment of surface tensions at equilibrium concentration as the silica nanoparticle concentrations increase. The first point of each silica nanoparticle concentrations being tested were initially dispersed in very low TX100 concentration, 0.01% and the equilibrium data shows the total loss of surfactant to the silica particles. As the surfactant amounts were depleted, the abrupt increase in surface tension convincingly proves the adsorption of TX100 on silica. Upon addition of more silica particles, surface tension increase rapidly reflected to the amount of surfactant monomers remained

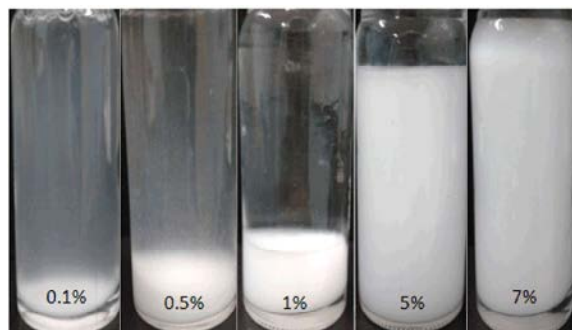


Fig. 1: Dispersion of silica in 0.1% TX100 at particles concentration of 0.1 to 7%.

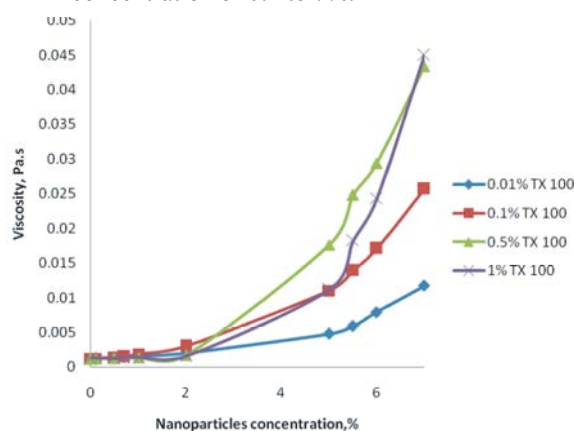


Fig. 2: Viscosities of silica/TX100 dispersion.

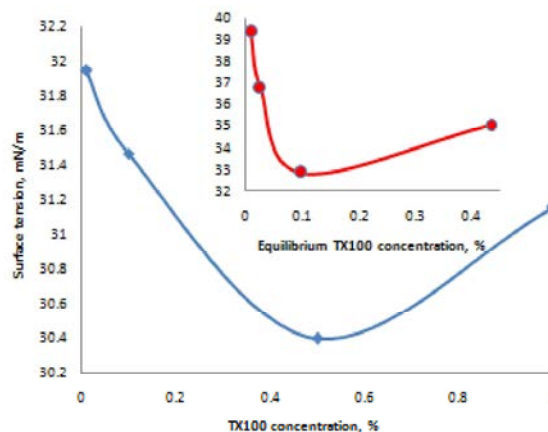


Fig. 3: Surface tension of TX100 solution taken at 0.01, 0.1, 0.5 and 1%. Inset: surface tension at the presence of 1% SiO_2 .

in the bulk dispersion to be attached at the air-water interfaces. Comparatively, the trend in surface tension reduction at 1% silica nanoparticles with the one studied by Hunter [21] was found to be slightly similar even with different type of particles hydrophobicity and this is probably due to the same non-ionic surfactant being

used. The same pattern was also found in the study by Cui [17] by using calcium carbonate, CaCO_3 nanoparticles in anionic surfactant concentration.

However, the presence of nanoparticles more or less did not transmute the pattern of surface tension reduction prominently though the equilibrium concentrations become more than half of the initial value. When 7% of SiO_2 was introduced in TX100 aqueous solutions, surface tension increase rapidly at lowest surfactant concentration and steeply reduced as the TX100 increased. Though this happened, surface tension of 7% SiO_2 in 1% TX100 solution seems to be lower than in lower bulk surfactant solution which indicates that the amount of monomers that lowering the surface energy is higher. The interaction of TX100-silica nanoparticles presented here in form of surface tension confirm the bulk dispersion activity and does not involve the addition or removal of any species to or from the system. Okubo [34] earlier on has identified the existence of silica nanoparticles alone in aqueous system does not show any significant changes to that of surface tension of the water which evinced the characteristic of the particles that is a non-surface active material.

Adsorption Isotherm of TX100 on SiO_2 : The mechanism of surfactant adsorption on particle surfaces takes place into several different manners which are due to; chemical bonding, hydrogen bonding, hydrophobic bonding and van der Waals forces [35]. As being defined by Condon [36], physisorption or generally means physical adsorption takes place due to the attractions between solute molecules and adsorbent which did not involve any chemical interaction except the relatively weak forces encountered at the surface of the solid by means of the hydrogen bonding and van der Waals forces. The properties of amorphous silica were investigated earlier on by Zhuravlev [37]. Theoretically, silica surfaces are inherently present with silanol groups, at which under adequate concentration on the surface, gives the silica hydrophilic properties and experimentally shown, density of silanol highly influence on the adsorption behaviour of solute species [38]. Upon interaction with adsorbates, the OH groups exist particularly act as centres of molecular adsorption of competently forming a hydrogen bond [37].

Adsorption isotherm of TX100 on silica was presented as in figure 4. At initial silica concentration of 0.1 and 0.5% the adsorption increase gradually with surfactant concentration with the amount of TX100 reduced about three-fifths the initial amount. Adsorption starts to increase rapidly at 1% silica, almost linearly at 5% and reverted to gradually again at 7% almost the same

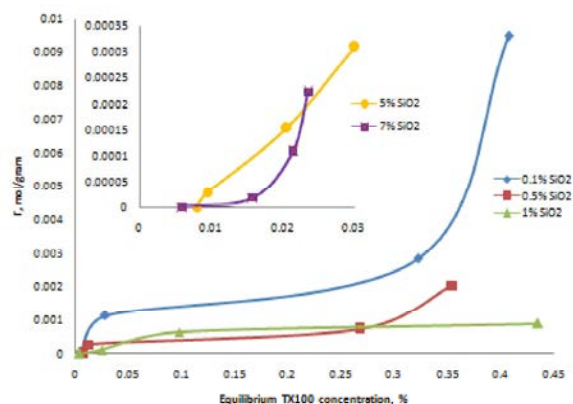


Fig. 4: Adsorption isotherm of TX100 on different concentration of SiO_2 at 25°C .

pattern obtained at lower silica particles but still absorbed the highest numbers of TX100 monomers. A reasonable explanation of these behaviours can be concluded; at low silica concentration, less surface contact area between solution and the particles take places and thus few amount of surfactants are being absorbed and the vice versa happened at higher silica concentration. Sudden drop in TX100 concentration can be seen at highest silica concentration with only about 2.5% of it left at equilibrium condition.

Surfactant adsorbed on silica surface are mainly governed by the initial interaction between silica surface and ethylene oxide head groups [39]. The mechanism of non-ionic adsorption was briefly discussed and summarized in previous study and was said to behave the same as of the ionic surfactant except for the sudden increase in adsorption at certain isotherm region due to the absence of electrostatic interaction [23]. Giles *et al.* [40-41] have demonstrated and classified theoretically and experimentally the behaviour of solute adsorption isotherm into few classes. The first three isotherms obtained from figure 4, (0.1, 0.5 and 1% SiO_2), yielding the characteristic of L class which refer to Langmuir isotherm behaviour; the most common type of adsorption that occurs to monodispersed or aggregated solute, reflected to the behaviour of surfactant monomers in aqueous systems [41]. With the slope of the graph represent the degree of difficulty of solute to find the vacant surface, the interpretation of the isotherm is; at lower silica concentration, the isotherm shows an increased in adsorption with increasing surfactant concentration due to the cooperative adsorption that are in progress at the surface available probably because of the compatible amount of both adsorbate and adsorbent. Hydrophobic characteristic on the adsorbent surface was found to develop when the isotherm obey L-curves [42].

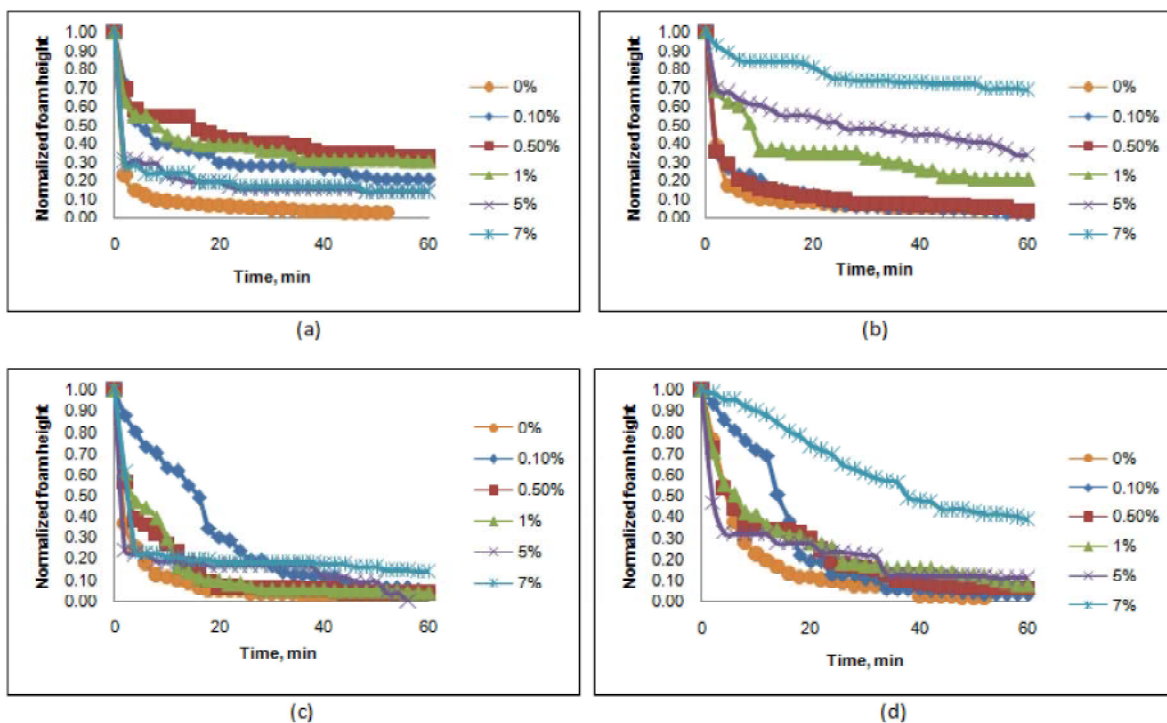


Fig. 5: Normalized foam height at initial TX100 of (a) 0.01%, (b) 0.1%, (c) 0.5% and (d) 1% in combined with various silica concentrations.

When the aqueous TX100 system was introduced with 5% silica, the plotted graph goes after C-curve, a linear isotherm where the surface procurable for adsorption is directly proportional with TX100 solute [40]. It is also been suggested that, the solute would probably continuously penetrated in the pore structure of silica particles which remain constant until it is completely filled. At even higher solid fraction in the dispersion, isotherm gives the characteristic of S-curve; surface turned expeditiously hydrophobic with augmentation in adsorption [42]. The adsorption of TX100 at the silica surface can also be related to the flocculation phenomena view as the phase separation occurrence in the bulk dispersion [20]. Earlier observation during dispersion preparation, it was found that the particles are completely flocculated as it is being mixed in the aqueous TX100 solution (Figure 1). As the agglomeration occur, the total surface area of particles involved in adsorption process also being reduced and thus lower the degree of TX100 adsorption at lower surfactant concentration in (a) and (b) as it may prevent the molecules from diffusing between the particles. Experimentally studied earlier on [31, 43], the adsorption of TX100 on silica happened in two step; 1) formation of hydrogen bonding between silanol and oxygen atoms of oxyethylene chain and; 2) aggregation of the adsorbed molecules via hydrophobic interaction

which lead to surface micelles formation. As described elsewhere [43], adsorption of TX100 on silica is highly dependence on the pH of the dispersion which not been covered here.

Though the adsorption was experimentally testified to be occurs in this study, further action should be taken as to demonstrate until what extent does the surface of silica is covered with solute involved. It can only be said that the particles were imparted 'partially hydrophobic' due to the adsorption of surfactant.

Foamability and Foam Stability of Silica-TX100 Dispersion:

Foamability of silica/TX100 dispersion was illustrated in figure 6. At lower TX100 concentration, 0.01 and 0.1%, foamability of TX100 solution alone are greater than that of being added with silica. This observation marked that, for these combinations of particle/surfactant, the foamability is independent of dispersion viscosity and surfactant depletion, unlike the earlier study [20]. It is noticeable that the stability of foams did not fit to be characterized by using half-life methods since the time taken for half of the foam to decay occurs within short time although the remaining 20 to 40% of the foam height left in the column able to maintain for couple of hours. Figure 5 shows the normalized foam height of the foam within 60 minutes time.

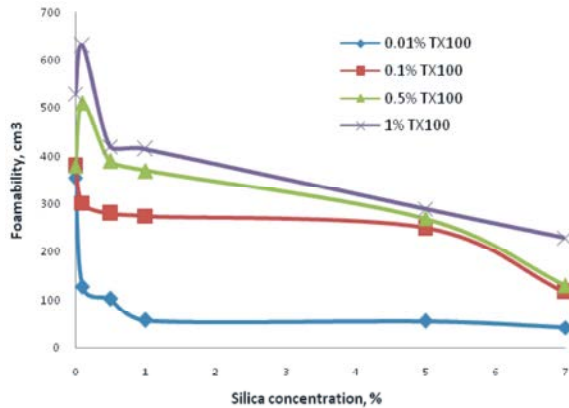


Fig. 6: Foamability of silica/TX100 dispersions. The initial TX100 concentrations are shown above.

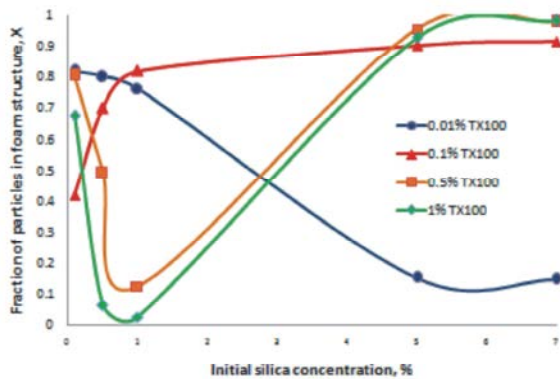


Fig. 7: Attachment of silica particles in foams structure as a function of silica concentration.

Foam stabilized with TX100 only decayed within less than 60 minutes for all tested concentrations with rapid fall immediately after foam generation. At initial TX100 concentration of 0.01%, normalized foam height increase steadily with increased of silica concentration from 0.1 to 1% and falls gradually as a function of time. At higher particles concentration foams height falls drastically within first few minutes. The foam shows an excellent stability both at lower particles and surfactant concentrations. At intermediate surfactant concentration, 0.1%, foam stability increase with increase in silica concentration. As being plotted in figure 7, fraction of particles attached in foam structure increase gradually with particles concentration, regardless either at the gas-water interfaces or trapped in the lamellae and plateau border because no microscopic observation have been conducted. This shows that the adsorbed TX100 happened to modified the surface of silica and able them to stabilize the foams. There is no significant change in normalized foam height pattern being observed on the foam generated from any silica concentrations tested and

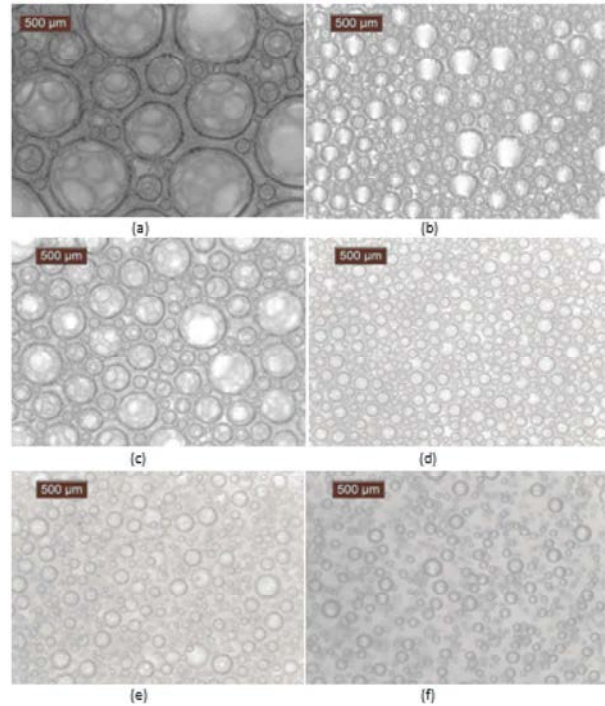


Fig. 8: Image of bubble stabilized by 0.1% TX100 (a) with 0.1% (b), 0.5% (c), 1% (d), 5% (e) and 7% (f) of silica nanoparticles.

0.5 and 1% TX100 combination. In both cases, foam stability reduced gradually at silica concentration from 0.1 to 1%. Figure 7 confirmed the stabilization trend from the attachment of silica in foam structure that is depleted almost linearly with the increase of particles concentration. Fraction reached maximum at higher particles concentration. It is predicted that the presence of particles under this condition happened to exist as a dense film in reducing the drainage rate in the thin film rather than attached at the gas-aqueous interfaces [20]. Figure 8 shows the image of foam stabilized by 0.1% TX100 and fraction of silica particles in it. Images were taken immediately after foams generation. TX100 only solution produced much larger bubble sizes compared to the TX100-silica solutions. As the silica concentration become higher, foam sizes become much smaller indicates the presence of particles in the foam structure. Mean diameter of the bubbles reduced from approximately 130 μm (0.1% SiO₂) to 75 μm (7% SiO₂). In the study by Zhang [20], they concluded that the coalescence and disproportionation of bubbles were avoided from the adsorption of modified particles on the bubble surfaces and the dense films around the bubbles resulting in smaller bubbles. Lower particle concentrations results in low adsorption rate of particles on bubble surface hence lead to unprotected bubble surfaces [44].

Foam generated by silica and 0.5% TX100 shows gradual decay trend at lower silica concentration. Decay pattern reduced abruptly at as the particles concentration increase as at 0.5 and 1%, the foam fraction left reached to that of foam stabilized by TX100 only solution. Upon introducing 5 and 7% silica, foam height falls immediately after the preparation and reached steady state condition for couple of hours. The behaviour of foams decay can possibly be explained by the adsorption of TX100 on silica. With increase in TX100 concentration, it is highly possible that the surface of silica rendered hydrophilic again at low silica concentration which unable them to stabilized the foams. Flocculation occurs at high silica concentration may lessen the synergetic effect in stabilizing the foams.

The experiments were further conducted without the presence of CO₂ gases. No significant changes in foam stability were observed.

CONCLUSIONS

From this experimental study, the following conclusions regarding aqueous foam stabilized by in-situ silica surface modification by TX100 were drawn;

- The in-situ adsorption of TX100 on silica surface exhibits certain criteria which highly dependent on the concentration of silica by mean of surface available for adsorption.
- The synergetic effect of silica/TX100 in stabilizing the foam occurs mainly at low and intermediate TX100 concentration.
- Lower TX100 concentration (0.01%) generated highly stable foams at low silica concentration.
- At intermediate TX100 concentration (0.1%), foams are much stable at higher silica concentration.
- Insignificant synergetic effects of silica/TX100 in stabilizing foams were observed at high TX100 concentration.

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