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CO₂ foam properties and the stabilizing mechanism of sodium bis(2-ethylhexyl)sulfosuccinate and hydrophobic nanoparticle mixtures

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Abstract: In this work, we have prepared of CO₂-in-water foam by mixing partially hydrophobic SiO₂ nanoparticles and sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and studied its properties. Observation of the appearance of the foam revealed that, with the continuous addition of AOT, the phase behavior of the SiO₂ nanoparticle and AOT mixed system transformed from that of a two-phase system of aggregated nanoparticles to that of a uniform dispersed phase. Both foaming ability and foam stability were optimized when the nanoparticles and the AOT were mixed in a proportion of 1:5. On the basis of our findings from measurements of the dispersion properties, including measurements of the adsorption isotherm of the surfactant on the nanoparticles, zeta potentials, interfacial tension and the three-phase contact angle, we concluded that the synergistic interactions between the SiO₂ nanoparticles and the AOT led to the adsorption of nanoparticles around the bubble surface and the formation of a spatial network structure of nanoparticles in the film, thereby enhancing the mechanical strength of the bubble and improving the resistance to outside disturbances, deformation and drainage. Laser scanning confocal microscopy (LCSM) analysis of the same foams further confirmed the existence of a “viscoelastic shell” wrapped around and protecting the bubble.

Keywords: AOT; adsorption; carbon dioxide; foaming ability; foam stability; SiO₂ nanoparticles

1. Introduction

Enhanced oil recovery (EOR) using carbon dioxide (CO₂) as displacement agent has become a popular option in oil-and-gas field development, particularly in miscible flooding areas, where as much as 20% of the original oil could be recovered in place.¹ However, CO₂ usually flows along high-permeability zones or fractures; thus, the oil in the low-permeability zones cannot be displaced effectively.²³ Moreover, CO₂, as a consequence of its low density and low viscosity compared with oil and water, often rises too high in the reservoir (gravity override) or fingers unevenly, resulting in poor sweep efficiency.⁴⁶ The formation of foams is a promising method to increase the apparent viscosity of CO₂ in porous media by wrapping the gas into bubbles in an aqueous foam.⁷¹⁰ It has been used in site applications since the 1960s in China and has already
been developed into a series of oil-displacement techniques after more than 50 years of practical application.\textsuperscript{11} However, foam is actually a thermodynamically unstable system.\textsuperscript{12} Therefore, foam stability is a key factor in this application.

Recently, foams stabilized by nanoparticles have received special attention in areas such as food-making processes,\textsuperscript{13} flotation,\textsuperscript{14} water-borne coatings\textsuperscript{15}, and EOR.\textsuperscript{16,17} An advantage of nanoparticles for the stabilization of foams is that they can irreversibly adsorb at CO\textsubscript{2}/water interfaces, potentially providing greater long-term stability than traditional surfactants that dynamically adsorb and desorb at the interface.\textsuperscript{18-20} Even more importantly, nanoparticles can be produced from chemically stable, abundant, inexpensive, and environmentally benign materials.\textsuperscript{21-23}

Not all types of nanoparticles can stabilize CO\textsubscript{2}-in-water foams with surfactants acting in synergy.\textsuperscript{24} The research on the compatibility between nanoparticles and surfactants is helpful for directing the optimum use, and the hydrophilic/CO\textsubscript{2}-philic balance (HCB) of the nanoparticles and surfactants is a key factor for optimization.\textsuperscript{25-27} For instance, surfactants with low HCBs have been used to stabilize water-in-CO\textsubscript{2} (W/C) microemulsions\textsuperscript{28-30} and emulsions,\textsuperscript{31,32} whereas surfactants with high HCBs stabilize CO\textsubscript{2}-in-water (C/W) emulsions\textsuperscript{33,34} and foams.\textsuperscript{35}

Conventional SiO\textsubscript{2} nanoparticles are too hydrophilic to stabilize C/W foams; thus, surface modification via the formation of covalent bonds has been used to lower the HCB.\textsuperscript{36,37} Numerous chemical agents can be used to modify nanoparticle surfaces, including CO\textsubscript{2}-philic fluorinated ligands, hydrophobic dichlorodimethylsilane (DCDMS), amphiphilic poly(ethylene glycol) (PEG), etc.\textsuperscript{38-41} Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) is a unique anionic surfactant that contains a twin hydrocarbon tail. It has been widely used to be solubilized in super critical CO\textsubscript{2} (sc-CO\textsubscript{2}) and form W/C reverse microemulsions with a certain amount of co-solvent\textsuperscript{42,43}. Water is readily solubilized in the polar core of the reverse microemulsions to form a “water pool”, which has been extensively used as a novel microreactor for carrying out many kinds of chemical and biochemical reactions\textsuperscript{44-46}. AOT reverse microemulsions formed in sc-CO\textsubscript{2} are thermodynamically stable aggregates of the amphiphilic surfactant, resulting in a hydrophilic head group region surrounding a nanosized water core with hydrophobic tails extending into a non-polar continuous phase.\textsuperscript{47} In contrast to W/C reverse microemulsions, the stable C/W foams can also be formed by AOT with a certain amount of SiO\textsubscript{2} nanoparticles. Here, we investigate the properties of a C/W foam prepared using partially modified SiO\textsubscript{2} nanoparticles and the surfactant AOT. First, the properties of SiO\textsubscript{2}/AOT aqueous dispersions are described and discussed systematically in relation to surfactant adsorption, nanoparticle wettability and zeta potential. Then, the properties of foams prepared by SiO\textsubscript{2}/AOT aqueous dispersions are studied, including their foaming ability and foam stability. In addition, the collaborative mechanisms of SiO\textsubscript{2}/AOT in stabilizing a foam are discussed. We hope that this study will promote the application of nanoparticle-stabilized foams in other similar oil-related fields.

\textbf{2. Experimental Section}

\textbf{2.1. Materials}

CO\textsubscript{2} (99.999\% purity) supplied by Tianyuan, Inc. (China) was used as received. Water was first passed through an Elga reverse-osmosis unit and then a Milli-Q reagent water system. Sodium hydroxide (96\% purity) provided by Sinopharm Chemical Reagent Co., Ltd. (China) was used to adjust the aqueous-phase pH. AOT (minimum 99\%, MW 444.56) purchased from Sigma Chemical
Co., Ltd. (USA) was vacuum dried at 60 °C for 24 h and stored in a vacuum desiccator prior to use. The critical micelle concentration \((\text{cmc})\) in water at 25 °C was 2.5 mM. Hydrophobic SiO\(_2\) nanoparticles (HDK, H18, 99.8% purity) were supplied by Wacker Chemical Co., Ltd. (Germany). It is a white powder consisting of nearly spherical particles with an average diameter of approximately 12 nm. The hydrophobic SiO\(_2\) nanoparticles were modified with DCDMS, and the silanol group density was approximately 0.5/nm\(^2\). The specific surface area was approximately 120 m\(^2\)/g. Its weight loss was less than 0.6 wt% after being dried for two hours at 105 °C. The point of zero charge (P.Z.C.) of the hydrophobic SiO\(_2\) nanoparticles, which was measured by the zeta-potential method, was 4.6. Experiments were conducted at room temperature unless otherwise specified.

2.2. Preparation and characterization of the SiO\(_2\)/AOT aqueous dispersions

To produce well-dispersed aqueous suspensions, the SiO\(_2\)/AOT dispersions were prepared by first adding the hydrophobic SiO\(_2\) nanoparticles into a certain concentration of AOT solution and then sonicating the resulting mixture with a 2000-W ultrasonic processor (YP-S17, 20 kHz, volume processing capacity: 0-2000 mL, Hangzhou Success Ultrasonic Equipment Co., Ltd. (China)) at an operating frequency of 20 kHz for 10 min to disperse the nanoparticles. The work-time and rest-time intervals for sonication were both set at 10 s to avoid overheating and foaming. Cold water was circulated through the container jacket using refrigerating and heating circulators (F12-EH, JULABO Labortechnik GmbH Co., Ltd. (Germany)) to maintain the temperature of the aqueous dispersions at 25 °C. The initial pH values of the SiO\(_2\)/AOT aqueous dispersions ranged from 5.58 to 6.53; the pH was adjusted to 9.8 by adding sodium hydroxide to give the particles an appreciable negative charge.

2.3. Adsorption of AOT onto the SiO\(_2\) particles

Ten milliliters of the prepared dispersion was centrifuged (GT10-1, Beijing Shidai Beili Centrifuge Co., Ltd. (China)) at 8000 rpm for 60 min. The concentration of AOT in the supernatant was analyzed by the TOC technique. The adsorption amount was then calculated as the difference between the initial concentrations divided by the mass of the dried solid.

2.4. Stability of the SiO\(_2\)/AOT aqueous dispersions

Twenty milliliters of prepared dispersion was first transferred into a 25 mL colorimetric tube. The phase behavior of the dispersions was then observed after 1 week.

2.5. Zeta potential of SiO\(_2\)/AOT aqueous dispersions

The zeta potential of the SiO\(_2\)/AOT aqueous dispersions was measured using a Malvern Zetasizer (Nano ZS90, Malvern Instruments, Ltd., UK). The equilibrated dispersion was sonicated for 10 min and then transferred into a disposable cell for zeta-potential measurement. The cell was maintained at 25 °C for 120 s. Each sample was measured at least 5 times, and the results were averaged. The zeta potential values were calculated according to the Smoluchowski equation.

2.6. Three-phase contact angle of particles

The classic captive drop method was used to measure the three-phase contact angle of the SiO\(_2\) particles. The prepared dispersion was first centrifuged (GT10-1, Beijing Shidai Beili Centrifuge
Co., Ltd. (China)) at 8000 rpm for 60 min. The lower layer was then washed with water to remove the unabsorbed AOT molecules and subsequently dried at 60 °C to yield particles. The particles were crushed into a powder that was then compressed into a circular disk. The three-phase contact angle of the disk was directly measured using a drop-shape tensiometer (Tracker-H, Teclis Co., France). Each sample was measured at least 5 times, and the results were averaged.

2.7. Properties of CO\textsubscript{2} foams generated from SiO\textsubscript{2}/AOT aqueous dispersions

To produce the CO\textsubscript{2} foams, experiments were conducted in a fume hood that was fully filled with CO\textsubscript{2} at ambient pressure unless otherwise specified. CO\textsubscript{2} foams were first prepared using 100 mL of SiO\textsubscript{2}/AOT aqueous dispersion and a Warning blender (GJ-3S, Qingdao Senxin Machinery Equipment Co., Ltd., China) operated at 8000 rpm for 3 min. The generated foam was immediately transferred into a glass cylinder to record the change of foam volume over time.

The properties of the CO\textsubscript{2} foam were also characterized using a Foamscan apparatus (Teclis Co., France). The development of the foam over time and the liquid content in the foam were observed by CCD cameras and conductivity measurements, respectively.\textsuperscript{51,52} The foams were generated by injecting CO\textsubscript{2} at the required flow rate through a porous glass disc (pore diameter 0.2–0.4 µm) at the bottom of a glass tube containing 60 mL of SiO\textsubscript{2}/AOT aqueous dispersion. Three pairs of electrodes on the inner-wall of the glass tube were used to measure the volume of the liquid. The development of the bubble size was observed by a CCD camera every 20 s. The CO\textsubscript{2} injection was stopped when the foam volume reached 200 mL; the evolution of the foam was then analyzed.

2.8. Interfacial tension measurements

![Fig. 1. Schematic of the combined pendant-droplet dynamic tensiometer and surface dilational rheometer.](image)

The interfacial tension (IFT) was measured through a drop-shape tensiometer (Tracker-H, Teclis Co., France). A schematic of the instrument is shown in Fig. 1. The main parts of the instrument include a dosing system, a light source, a CCD camera, a frame grabber, a needle for drop formation and a high-pressure fixed-volume view cell consisting of a stainless steel block with two sapphire windows. Thus, the drop shape could be observed through the windows using the CCD camera. The volume of the view cell was 400 cm\textsuperscript{3}, and it could withstand a maximum pressure of 20 MPa.

Before the measurement, the view cell was fully filled with CO\textsubscript{2} at ambient pressure. A pendant drop of the aqueous dispersion was then formed at the end of a stainless steel needle attached to a gas-tight syringe. When a new drop formed, the drop-shape apparatus provided automatic
feedback of the drop area and drop volume during the experiments. Thus, the dynamic $I_F T$ was recorded through axisymmetric drop-shape analysis. Droplets of the dispersions were maintained for 10 min to reach a steady $I_F T$. The dosing system, controlled by the computer, then triggered periodical oscillations at a certain frequency and a volume amplitude of $1 \mu m^3$ and measured the corresponding changes in the $I_F T$. The drop shape, drop volume and area were recorded by the CCD camera and were subsequently analyzed using commercially available drop-image software. The viscoelasticity, which was originally proposed by Gibbs, was given by

$$
\varepsilon = \frac{d\gamma}{d \ln A}
$$

where $\varepsilon$ is the interfacial dilational viscoelasticity, $\gamma$ is the interfacial tension, and $A$ is the interfacial area. This parameter gives the interfacial resistance to changes in area or volume, which directly affects the foam stability. Details about the tensiometer and methods are available elsewhere.  

3. Results and Discussion

3.1. Properties of SiO$_2$/AOT aqueous dispersions

Because of the hydrophobic properties of the SiO$_2$ nanoparticles (the air-water-SiO$_2$ contact angle is 122°), a 2000-W ultrasonic processor was used to disperse the SiO$_2$ nanoparticles into AOT solutions. The effect of sonication on the SiO$_2$/AOT aqueous dispersions is shown in Fig. 2. The SiO$_2$ nanoparticles present in the conventional stirred aqueous dispersions were obviously aggregated. Under the influence of high-intensity ultrasonic cavitation, the aggregated SiO$_2$ nanoparticles were impacted by the surfactant-enriched water droplets of micron size because of cavitation forces. The aggregation of the nanoparticles was significantly decreased, thus providing more opportunities for the nanoparticles to contact the surfactant. Ultrasonic cavitation could be a better choice for the preparation of SiO$_2$/AOT aqueous dispersions.

![Fig. 2. TEM images of conventional stirring aqueous dispersions and ultrasound-assisted aqueous dispersions.](image)

Because the hydrophobic SiO$_2$ nanoparticles were modified with dimethyl siloxane, the P.Z.C. of the hydrophobic SiO$_2$ nanoparticles was 4.6. To induce a high particle surface charge, concentrated NaOH was subsequently added to adjust the pH of the SiO$_2$/AOT aqueous dispersion to 9.8. At a fixed particle concentration of 1 wt%, the addition of AOT led to a dramatic change in the stability of the aqueous dispersions. Fig. 3 illustrates that, when the AOT concentration was low, the phase separation of the dispersive system was obvious because of the hydrophobicity of the particles. As a result, the flocculated particles accumulated at the bottom of the test tube. As
the AOT concentration was increased, the sedimentation extent began to decrease and the liquid of the top layer became turbid. When the concentration was increased to 0.40 wt%, flocculent particles were dispersed completely and the dispersive system became color uniform. It is likely that the adsorption of AOT on SiO$_2$ nanoparticles improves their dispersion stability.

**Fig. 3.** Photograph of the SiO$_2$/AOT aqueous dispersions. (The AOT concentrations are shown in the picture (wt%); the particle concentration is fixed at 1.0 wt%).

Zhang et al. and Binks et al. both studied the adsorption of surfactants with opposite charges onto hydrophilic particles, which have changed the dispersion properties of nanoparticles. They demonstrated the existence of a monolayer or a bilayer of surfactants on the particle surface, where the surfactant molecules were adsorbed by electrostatic attraction. The formation of the monolayer or bilayer could change the wettability of the particles, which could also make the particles adsorb and remain at the surfaces of air bubbles, stabilizing the foam.

In order to verify the extent of AOT adsorption on hydrophobic SiO$_2$ nanoparticles surfaces, we have determined the adsorption isotherm using the depletion from solution method and the results are shown in Fig. 4 (a). There is a gentle increase in the adsorbed amount initially followed by a more significant increase at higher concentrations, ending close to the cmc, which can be described as an “S”-type isotherm with three regions. Meanwhile, because the zeta potential of nanoparticles directly reflects the adsorption of surfactant onto nanoparticles, electrophoretic measurements were performed with SiO$_2$ dispersions as a function of the AOT concentration, the results are presented in Fig. 4 (b). The zeta potential in the absence of surfactant is -7.12 mV at this high pH. The addition of AOT gradually decreases the potential at 0.17 mM, after which the potential significantly decreases until 5.47 mM, which can also be divided into three regions. The adsorption of AOT on the SiO$_2$ nanoparticles surfaces is mainly controlled by the electrostatic forces and hydrophobic interactions. In region I, the zeta potential of nanoparticles is so small (about -10 mV) that the hydrophobic attractive interaction between the twin hydrocarbon tails of AOT and the modified nonpolar groups of nanoparticles is dominant here, hence, AOT monomers adsorb individually with their polar groups extending into the bulk and decrease the zeta potential of nanoparticles. In region II, the aggregated nanoparticles start to disperse when the zeta potential of nanoparticles decreased to a certain degree. Once the aggregated nanoparticles have dispersed, which will increase the amount of available area for AOT monomers to adsorb on. Meanwhile, the polar head of the AOT will be oriented away from the surface of the nanoparticles due to electrostatic repulsion, resulting in a greater probability of the twin hydrocarbon tails contacting...
the nonpolar group on the surface of the nanoparticles. As a result, there is a significant increase of the adsorption of AOT monomers on the nanoparticles surfaces and the magnitude of the potential of nanoparticles. In region III, the adsorbed amount reaches a plateau value and the nanoparticles are well dispersed.

![Fig. 4. Adsorption isotherm of AOT surfactant on the hydrophobic SiO$_2$ nanoparticles in water (a) and Zeta potential of SiO$_2$/AOT aqueous dispersions (b) (the SiO$_2$ concentration are both 1.0 wt%); pH = 9.8.](image)

The wettability of the particles is generally described by their contact angle, which is an important piece of evidence in determining the adsorption of AOT at the particle surfaces. The variation of the three-phase contact angle values of the SiO$_2$ particles with increasing AOT concentration is shown in Fig. 5. In the absence of the surfactant at this high pH, the contact angle of the SiO$_2$ particles is 122°, indicating that the particles are hydrophobic. Increasing the AOT concentration results in a decrease in contact angle to a minimum of 73°. The SiO$_2$ particle surfaces thus undergo a transition from hydrophobic-to-intermediate wettability to hydrophilic wettability, which confirms that the AOT monomers are adsorbed onto the SiO$_2$ nanoparticles surfaces with the polar groups extending into the bulk due to the hydrophobic attractive interaction between the twin hydrocarbon tails of AOT and the modified nonpolar groups of SiO$_2$ nanoparticles.

![Fig. 5. Three-phase contact angle of SiO$_2$ particles (1.0 wt%) as a function of the AOT concentration; pH = 9.8.](image)
3.2. Foaming ability of SiO$_2$/AOT aqueous dispersions

The foam volumes of the SiO$_2$/AOT aqueous dispersions are shown in Fig. 6. The AOT concentration in the dispersion is expressed by a relative concentration ($RC$, wt%/wt%), which refers to the ratio between the AOT concentration and the SiO$_2$ concentration in the dispersions, unless otherwise specified. The concentrations of SiO$_2$ in the dispersions investigated were 0.5, 1.0, 1.5, and 2.0 wt%, and the AOT concentrations were varied from $RC = 0$ to 1 at each nanoparticle concentration. The foam volume increased with increasing concentration of SiO$_2$ nanoparticles at concentrations below 1.5 wt%. A further increase of the SiO$_2$ concentration, however, resulted in a significant decrease of the foam volume; the foam volume of SiO$_2$ at 2.0 wt% was even lower than that of SiO$_2$ at 0.5 wt%. For each nanoparticle concentration, the foam volume increased gradually with increasing AOT concentration and reached a maximum at the same AOT/SiO$_2$ concentration ratio ($RC = 0.4$).

![Fig. 6. Foam volume of SiO$_2$/AOT aqueous dispersions as a function of the relative AOT concentration ($RC$) at different SiO$_2$ concentrations.](image)

To study the mechanism of the foaming ability, the IFT of the SiO$_2$/AOT aqueous dispersions with CO$_2$ were investigated; the results are shown in Fig. 7(a). For each nanoparticle concentration, the IFT value decreased gradually with increasing AOT concentration and exhibited an inflection point at the same AOT/SiO$_2$ concentration ratio ($RC = 0.4$), which is defined as the cmc of AOT. The schematic illustration of the synergistic influence mechanism of SiO$_2$/AOT on the IFT is shown in Fig. 8. In region I, the concentration of AOT is lower, and the AOT monomers mainly adsorb into the CO$_2$/liquid surface, as a result, the amount of AOT monomers in the bulk is small. At this stage, the main factor affecting the IFT values is AOT monomers at the surface. Hence, the IFT value decreases gradually with increasing AOT concentration. In region II, there are sufficient AOT monomers to aggregate in the bulk with the continuing increases of AOT concentration. Though both AOT monomers and SiO$_2$ nanoparticles have the same negative charge, the hydrophobic attractive interaction between the twin hydrocarbon tails of AOT monomers and the modified nonpolar groups of nanoparticles still promote the migration of AOT monomers to adsorb onto the surface of SiO$_2$ nanoparticles. This phenomena has been discussed in detail for the interaction of surfactant with hydrophobically modified polymers$^{57,58}$, which was also dependent on the hydrophobic attractive interaction. Meanwhile, the electrostatic repulsion between AOT monomers and SiO$_2$ nanoparticles keeps the hydrophilic head group of AOT monomer away from
SiO$_2$ nanoparticles surface, which promotes the contact between the hydrophobic tails of AOT monomers and SiO$_2$ nanoparticles. In related investigations\textsuperscript{59-61}, the effect of alcohols and urea on micelle formation has been found to increase the $cmc$ due to the diminishing of the hydrophobic effect. Similarly, the adsorption of AOT monomers on SiO$_2$ nanoparticles will diminish the hydrophobic effect of AOT monomers in solution, that is, it would hinder the micellization of AOT monomers, leading to an increase of the $cmc$ of AOT, as shown obviously in Fig. 7(a). In region III, the nanoparticle-nanoparticle electrostatic repulsion increases due to the decreased zeta potentials of nanoparticles, which will promote the dispersion of nanoparticles in the bulk, in agreement with the results in Fig. 4(b). Caused by the adsorption of AOT monomers, the polar groups are introduced into the surfaces of SiO$_2$ nanoparticles. It will change the wettability of parts of the dispersed SiO$_2$ nanoparticles from hydrophobic to amphiphilic: the nonpolar group on the surface of the nanoparticles adsorbed with AOT monomers shows hydrophilic, whereas the nonpolar group without adsorption of AOT monomers still shows hydrophobic. Therefore, the dispersed nanoparticles shows a tendency to adsorb upon the CO$_2$/liquid surface because of the hydrophobicity\textsuperscript{62,63}, and the IFT value are still decreasing because of the surface active. Meanwhile, the AOT monomers will bend towards to the liquid to ensure that the polar group will extend into the liquid. Only in this way can the nanoparticles adsorbed on the CO$_2$/liquid surface with low interfacial energy. In region IV, with the continuing increases of AOT concentration, AOT monomers dispersed in the bulk tend to adsorb onto the surface of the other parts of the dispersed SiO$_2$ nanoparticles, which will cause these nanoparticles to be hydrophilic rather than amphiphilic, and hinder the migration of these nanoparticles to adsorb on the CO$_2$/liquid surface. Then, the IFT reaches a plateau value. It can also be seen that the IFT values of the SiO$_2$/AOT aqueous dispersions decrease with increasing SiO$_2$ concentrations, whereas the SiO$_2$ concentration at 2.0 wt\% is just slightly lower than the IFT of the SiO$_2$ concentration at 1.5 wt\%. It indicates that the more SiO$_2$ nanoparticles introduced, the more advantageous for the formation of amphiphilic particles. However, when the CO$_2$/liquid surface contains the maximum number of the amphiphilic particles allowed, AOT monomers will be adsorbed at the surface of the excess amphiphilic particles, induce the transformation of these nanoparticles from amphiphilic to hydrophilic, which will facilitate the stable dispersion of these nanoparticles in the bulk, but do not affect the IFT values of the SiO$_2$/AOT aqueous dispersions.

The above situations indicate that a synergistic effect occurs between the nanoparticles and the AOT to reduce the IFT values of the SiO$_2$/AOT aqueous dispersions, which implies that the formation of foam requires less energy, thus improving the foaming ability. Moreover, as shown by Xu et al.\textsuperscript{64}, the lower IFT can reduce the probability of foam rupture and create more successful foaming. Thus, the addition of SiO$_2$ nanoparticles to the AOT solution can facilitate the formation of a protective film at the CO$_2$/dispersion surface and promote the formation of foam.

It can also be seen that a significant decrease in the foam volume was observed when the concentration of SiO$_2$ nanoparticles was increased from 1.5 wt\% to 2.0 wt\%, whereas the IFT at an SiO$_2$ concentration of 2.0 wt\% was only slightly lower than that at 1.5 wt\%. This scenario was corroborated by viscosity measurements of the SiO$_2$/AOT aqueous dispersions. As reported by Zhang et al.\textsuperscript{65}, dispersions with increased viscosity require greater energy to produce a foam. Fig. 7(b) highlights the influence of the SiO$_2$ and AOT concentrations on the viscosity of the dispersions. The viscosity significantly increased when the concentration of SiO$_2$ nanoparticles was increased from 1.5 wt\% to 2.0 wt\%, whereas the viscosity only slightly increased when the
The concentration of SiO$_2$ nanoparticles was increased below 1.5 wt%. Therefore, these two factors both influence the foaming ability. When the change in viscosity is small, the $IFT$ of the SiO$_2$/AOT aqueous dispersions with CO$_2$ is dominant; in contrast, the viscosity is dominant when the viscosity changes significantly.

**Fig. 7.** The $IFT$ of SiO$_2$-AOT aqueous dispersions with CO$_2$ (a) (Insert: the $cmc$ of AOT at different SiO$_2$ concentrations) and the viscosity of SiO$_2$-AOT aqueous dispersions (b) as a function of the relative AOT concentration ($RC$) at different SiO$_2$ concentrations.

**Fig. 8.** The schematic illustration of the synergistic influence mechanism of SiO$_2$/AOT on the $IFT$.
3.3. Foam stability of SiO$_2$/AOT aqueous dispersions

The stability of the foams in the SiO$_2$/AOT dispersions was also observed to vary with nanoparticle concentration and surfactant concentration. As illustrated in Fig. 9, the most stable foams of each nanoparticle concentration were all formed at the same concentration ratio of AOT to SiO$_2$ (i.e., $R_C \approx 0.2$). As shown in the three-phase contact-angle plot in Fig. 5, this value corresponds to nanoparticles of intermediate wettability with the contact angle nearest to 90°. The nanoparticles can adsorb onto interfaces (water-CO$_2$) with a suitable contact angle $\theta$ between the nanoparticle and the interface$^{66}$: If $\theta$ measured into the aqueous phase is normally $< 90^\circ$, then a larger fraction of the nanoparticle resides in the water than in the CO$_2$. Conversely, the nanoparticles reside more in the CO$_2$ than in the water when $\theta > 90^\circ$. Accordingly, the ratio of surfactant adsorption onto the nanoparticles is optimal when $\theta = 90^\circ$, resulting in the optimal surface activity of the SiO$_2$ nanoparticles coated with AOT (Fig. 7 (a)). The adsorption of partially coated nanoparticles onto air-bubble surfaces may be responsible for this optimal activity. Moreover, some researchers$^{66}$ also reported that the relevant parameter of foam stability is the desorption energy $E$, which is the energy required to remove the nanoparticle from the interface and is given by

$$E = \pi R^2 \gamma_{a\beta} (1 - |\cos \theta|)^2 \tag{1}$$

where $R$ and $\gamma_{a\beta}$ are the radius of the nanoparticles and the IFT of gas and water, respectively.

Eq. (1) shows that the nanoparticle is most strongly held at the interface when $\theta = 90^\circ$, which maximizes $E$. The particles adsorb around the bubble surfaces, which form the nanosized particulate films; the particles can thus inhibit the coalescence, disproportionation, and film drainage. Consequently, the stability of the foam is improved.

![Fig. 9](image_url) Half-life of foams stabilized by the SiO$_2$/AOT system as a function of the relative AOT concentration ($R_C$) at different particle concentrations indicated in the legend (wt%).

To confirm the adsorption of the nanoparticles around bubbles, we developed the technique of studying freshly prepared foams using SiO$_2$/AOT aqueous dispersions with laser scanning confocal microscopy (LSCM, Olympus Fluoview 500, Japan), as shown in Figs. 10(a) and (b). The concentrations of AOT and nanoparticles were fixed at 0.2 wt% and 1.0 wt%, respectively. The SiO$_2$ nanoparticles were first labeled with fluorescein isothiocyanate (FITC), and the
dispersion was subsequently washed with deionized water to remove the free FITC in the bulk. In order to observe the nanoparticles adsorbing on the bubble surface and dispersing in the bulk, we refocused LSCM on bubbles and bulk respectively, and superimposed the bright field image and fluorescence image under blue exciting light (Fig. 10). It can be observed that there are the adsorption of SiO$_2$ nanoparticles on the bubble surface (Fig. 10(a)) and the dispersion of SiO$_2$ nanoparticles in the bulk (Fig. 10(b)) at the appropriate concentrations of the nanoparticles and AOT, in conformity with the results in Fig. 8. The viscoelastic shell formed by the SiO$_2$ nanoparticles around the bubble surface exhibits enhanced mechanical strength to resist disturbances and deformation of the bubble$^{13}$. Meanwhile, the formation of a spatial network structure of SiO$_2$ nanoparticles dispersed in the foam film strengthens the ability of the film to withstand disturbances and drainage (Fig. 10(c)). Therefore, the stabilization of foams is facilitated.

![Fig. 10. Confocal fluorescence image of foams prepared with SiO$_2$/AOT aqueous dispersions, refocusing on bubbles (a) and bulk (b), (c) is the schematic illustration of the stabilization mechanism of SiO$_2$/AOT aqueous dispersions on the CO$_2$ foam film. (The AOT concentration is 0.2 wt%, and the nanoparticle concentration is fixed at 1.0 wt%).](image)

Fig. 11(a) shows a photograph of dried foams; these photographs were taken 24 h after the samples were prepared. The drained liquids became more opaque with increasing AOT concentration, which indicated that the nanoparticles changed from hydrophobic to intermediate wettability and then to hydrophilic wettability, in agreement with the results in Fig. 5. Meanwhile, the concentration of nanoparticles located in the dried foam phase decreased with increasing AOT concentration, and no dried foam residue was observed when the AOT concentration exceeded 0.2 wt%. This result indicates that the nanoparticles indeed played a role in stabilizing the foams at the proper AOT concentration by forming a three-dimensional network structure, as shown in Fig. 11(b). The existence of this spatial network gives the bubble structure its own “skeleton,” which enhances the mechanical strength of the bubble and also improves the resistance to outside disturbances. As a result, the stability of the bubbles is greatly improved.
Fig. 11. Photograph of dried foams prepared with SiO$_2$/AOT aqueous dispersions (a) and magnification of the red-circled area (b). (The AOT concentrations are shown in the picture (wt%). The nanoparticle concentration is fixed at 1.0 wt%.)

The morphology was studied with the Foamscan apparatus to confirm that the SiO$_2$ nanoparticles affect the foam stability with the AOT. Fig. 12 shows the morphology of a conventional aqueous foam and a SiO$_2$/AOT-dispersion-enhanced foam. The results show that a conventional aqueous foam with surfactant exhibits obvious inhomogeneity, with different sizes of bubbles that will easily merge into larger bubbles and finally form a single large bubble. Meanwhile, the film of the large bubble is very thin and can be easily ruptured, resulting in instability of the foam system. However, the foam becomes compact and uniform with the addition of the SiO$_2$ nanoparticles. The SiO$_2$ nanoparticles can form a viscoelastic shell around the bubble surface with AOT, as shown in Fig. 10. The viscoelastic shell can make the foam film become thicker and protect bubbles against shrinkage and coalescence.$^{14}$ As a result, the SiO$_2$/AOT dispersions enhance the foam stability.

4. Conclusions

A detailed investigation into the behavior of CO$_2$-in-water foams stabilized by a mixture of SiO$_2$ nanoparticles and AOT surfactant at high pH was conducted. A synergistic effect was demonstrated to occur through the combination of both increasing the foaming ability and
improving the foam stability. When both SiO$_2$ nanoparticles and AOT surfactant are mixed to prepare the foam, control of the quantities of the two species is important. Interfacial tension isotherms showed that the optimal ratio between the AOT concentration and the SiO$_2$ nanoparticle concentration contributed to improving the effective content of surfactants at the CO$_2$/liquid interface to achieve the best surface activity. The wettability of the nanoparticles was adjusted via the AOT concentration because of the hydrophobic attractive interactions; thus, an optimum ratio was selected to obtain a maximum desorption energy, which enhanced foam stability. A confocal laser-induced fluorescence detection technique revealed that the nanoparticles form a viscoelastic shell wrapped around the bubbles. This shell enhances the mechanical strength of the bubbles and improves its resistance to outside disturbances. The spatial network structure of SiO$_2$ nanoparticles dispersed in the foam film strengthen the ability of the film to withstand disturbances, bubble deformation and drainage.

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Notes
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