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Synergistic action of TiO₂ particles and surfactants on the foamability and stabilization of aqueous foams

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Small particles can be activated *via* a synergistic effect with surfactants and adsorbed to the air–water interface to generate and stabilize foams, which has been applied extensively to develop new materials and techniques. Here, we studied the synergistic effects of TiO₂ particles with ionic surfactant SDS (sodium dodecyl sulfate), ionic AOT (sodium di-2-ethylhexylsulfosuccinate), and cationic CTAB (cetyltrimethylammonium bromide) in aqueous solution, and their impacts on the foamability and foam stability were assessed by measuring the foam volume and observing the number of particles adsorbed onto the foam surface. The results showed the interactions of TiO₂ particles with SDS and CTAB surfactants were synergistic in both foamability and foam stability. The degree of synergy of the CTAB–TiO₂ mixed system was stronger than that of the SDS–TiO₂ mixed system as a whole. However, the interaction of TiO₂ with AOT (a double carbochain anionic surfactant) in the TiO₂–AOT mixed system was generally not synergistic. Unexpectedly, a maximum synergistic effect among these mixed systems occurred in the TiO₂–AOT system at an AOT concentration of approximately 5 mM. This study provides further understanding for the mechanism of foaming and stability of foam modulated by surfactant and colloidal particles and provides a useful reference for future applications.

Introduction

Foams stabilized with particles in aqueous surfactant solutions have brought significant technological impacts, including particles assembling at the air–liquid interface to form dry water (water in air)[1–3] and liquid marbles (large liquid droplets encapsulated in air),[4–6] as well as colloidosomes[7] and anisotropic particles.[8] Furthermore, this technology has been applied in industrial processes extensively. Oil recovery is enhanced using foam behavior mediated by the interaction between nanoparticles and mixed surfactant in brine solution.[9] Wastewater is cleared by removing hydrophobic contaminations that attach to air bubbles.[10] Porous ceramics and porous metals are fabricated using particle-rich foam precursors.[11] Therefore, a comprehensive understanding to the mechanism of foamability and foam stability mediated by surfactant and particles in aqueous solution would be beneficial to further practical applications.

Small particles (nanometres to several micrometres), with a suitable wettability at their surfaces, can be strongly attached to liquid–vapor or liquid–liquid interfaces, and thus behave as the foam or the macroemulsion stabilizers, respectively.[12–14] This process results in irreversible adsorption,[1,15] unlike that of surfactant molecules with adsorption and desorption on a rapid timescale. And this adsorption, namely, small particles accumulated at the two-phase interface need much higher adsorption free energies than the thermal energy kT.[15] Usually, particles promote their adsorption free energy *via* the activation of surface or the modification of surface wettability, which can be characterized by the contact angle of the particle at the aqueous side of the interface. There are three approaches to obtain higher surface activation for small particles or change their surface wettabillity in general. The first is to prepare "Janus" particles with asymmetric surface chemistry, *i.e.*, regionally hydrophilic on one side and hydrophobic on the other side.[16,17] The "Janus" particles, however, involve complicated preparation processes and are difficult to produce in large quantities. Another solution is to modify the wettability of the non-surface-active or low-surface-active small particles using a homogeneous surface coating, such as, modifying SiO₂ from extremely hydrophilic to very hydrophobic,[18] but the high cost of activating particles makes this method less commercially viable. The third is to use the interaction of amphiphilic compounds with particle to make surface active.[19,20] Surfactant, as typical amphiphilic compound, is usually added to solutions to change the activation of particles by the adsorption of surfactant molecules onto particle surface. This method is

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comparatively less complicated and less expensive, and is therefore practically significant.

Recently, Binks *et al.*[21] used surfactant SDS (sodium dodecyl sulfate) to successfully achieve the inversion of dry water to aqueous foam by changing the activation of silica surface particles in aqueous system, whereby the hydrophobic surface of the particle was converted into hydrophilic surface by adsorbing SDS molecules. AOT, an ionic surfactant with double carbon chain, was used as a usual charge control agent for particles charging in apolar dispersions[22,23] is considered for the activation of $CaCO_3$ nanoparticles and investigated their ability to stabilize aqueous foam.[24] Mineral oxide nanoparticles and cationic CTAB were investigated for their synergistic effect on stabilization of CO_2 foam for the application in enhanced oil recovery.[25] In addition, the mechanism of particle stabilizing aqueous foams was revealed by the synergy between SiO_2 particles and surfactants at different length scale.[26] Langevin and co-workers also studied the mechanism of foam stabilization based on the interaction of SiO_2 particles and surfactant in the mixed aqueous solution.[27] Nevertheless, although these works have described the surface of particle activated by the adsorption of surfactant to stabilize aqueous foams at the interface, the investigated objects mainly focused on anionic surfactant (SDS in particular), and SiO_2 particles but less involved for other surfactants and particles. As a common material, TiO_2 particles have very important applications in food, cosmetics, medicine and functional materials,[28–30] while the studies of TiO_2 particles in stabilizing aqueous foam are relatively inadequate. Therefore, the systematic investigation of the surface activation of TiO_2 particles by interaction with different surfactants in aqueous solution is advantageous to further understand the mechanism of particle stabilizing aqueous foams.

In this paper, we investigated the surface activation of TiO_2 by the interaction with anionic surfactants SDS, AOT (sodium di-2-ethylhexylsulfosuccinate), and cationic surfactant CTAB (cetyltrimethylammonium bromide) in aqueous solution. The synergistic interactions between TiO_2 particles and SDS, AOT, and CTAB in both foamability and foam stabilization were analyzed by measuring volume of foam and observing the adsorption of particle on the surface of foam. Possible reasons for the discrepancy of these synergistic effects of particles with these surfactants were suggested. The aim of this paper was to obtain a further insight into the activation of the particle *via* surface active agent to stabilize aqueous foam at water–air interface. Meantime, the study would also provide the references for potential applications of TiO_2-surfactant aqueous systems in relevant industries.

Methods

Materials

TiO_2 particles with a primary particle diameter of 110 nm were supplied by Sigma-Aldrich. The particles were originally delivered as a dispersion in deionized water. Obtaining dry particles needed a dehydration process through a multistage solvent swap using ethanol as an intermediate solvent, followed by

vacuum drying at 30 °C. Fig. 1 shows a scanning electron microscopy (SEM, Quanta 200, FEI) image of a dried aqueous dispersion of the particles, where the particles fused with each other and formed micron-sized agglomerates. SDS and CTAB (each 99% of purity) were from Shanghai Geneland Biotech Co., Ltd., China, and AOT of 99% purity was the commercial production of Sigma-Aldrich. All surfactants were used as received. Deionized water with a resistance of 18.2 MΩ cm at 25 °C was obtained using a deionized water system (LDD-01, Ludao, Shanghai, China).

Preparation of aqueous surfactant dispersions without and with TiO_2 particles

A series of different concentrations of surfactants (0.01–50 mM) were dispersed in deionized water. The dried TiO_2 particles were weighed and added into these aqueous surfactant solutions. The mixed solutions without and with particles were respectively sealed into 50 ml beaker and then dispersed using constant temperature magnetic stirrer (85-2, Changzhou, China) at 2400 rpm for 2–5 min.

Preparation and measurement of aqueous foams

The aqueous surfactant dispersion without TiO_2 particles (10 ml) was transferred to a 100 ml cylindrical graduated flask. The flask was stoppered and then shaken up and down vigorously about 30 times. The foam volume immediately after shaking and 30 min after shaking were recorded as V_0 and V_{30}, respectively. Similarly, a 10 ml dispersion of aqueous surfactant solution with TiO_2 particles was placed into a 100 ml cylindrical graduated flask with a stopper, and the same procedure was repeated, except shaking was performed 50 times to facilitate full interaction between particles and surfactants. And foam volume immediately after shaking was recorded as V_{0P}, and that 30 min after shaking was as V_{30P}. V_0 and V_{0P} were taken as the measure of foamability of aqueous surfactant solution without
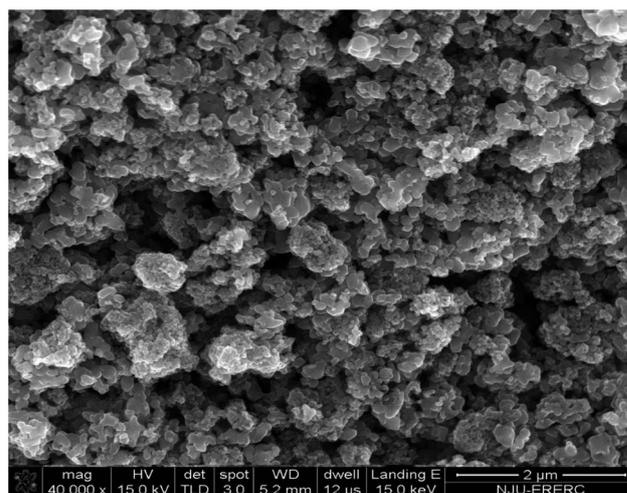

Fig. 1 SEM image of TiO_2 particles dispersed in pure water after drying.

and with particles, respectively. V_{30} and V_{30P} were the measure of foam stability of aqueous surfactant solution without and with particles, respectively. These experiments were repeated three times.

Characterization of aqueous foams with optical microscopy

To observe foams stabilized by a surfactant alone and by a combination of TiO_2 particles and surfactants, each 5 ml dispersion was transferred to a 10 ml bottle and aerated at 5000 rpm for 5 min using a YSDF-400 centrifuge (Yuesheng, Shanghai). The foam was removed and placed on a microscope slide (without coverslip), and micrographs were taken (before moisture evaporated) using a Motic BA400 microscope system (Motic, Xiamen).

Results

Fig. 2 showed foam volumes, as the function of surfactant concentration, in aqueous solution with SDS alone immediately after shaking (V_0), SDS alone 30 minutes after shaking (V_{30}), SDS plus TiO_2 immediately after shaking (V_{0P}), and SDS plus TiO_2 30 minutes after shaking (V_{30P}), the particle concentrations of which were 0.01% (Fig. 2a) and 0.5% (Fig. 2b). Foam volumes were all small at SDS concentrations below 0.5 mM with and without TiO_2 particles in Fig. 2. Beyond this concentration, the foam volumes with SDS alone (V_0 and V_{30}) increased quickly at first, and reached a maximum peak value near the concentration of 8 mM, which is the critical micelle concentration (CMC) of SDS in pure water,[31] then decreased with further increase of SDS concentration. For the TiO_2 particle concentration of
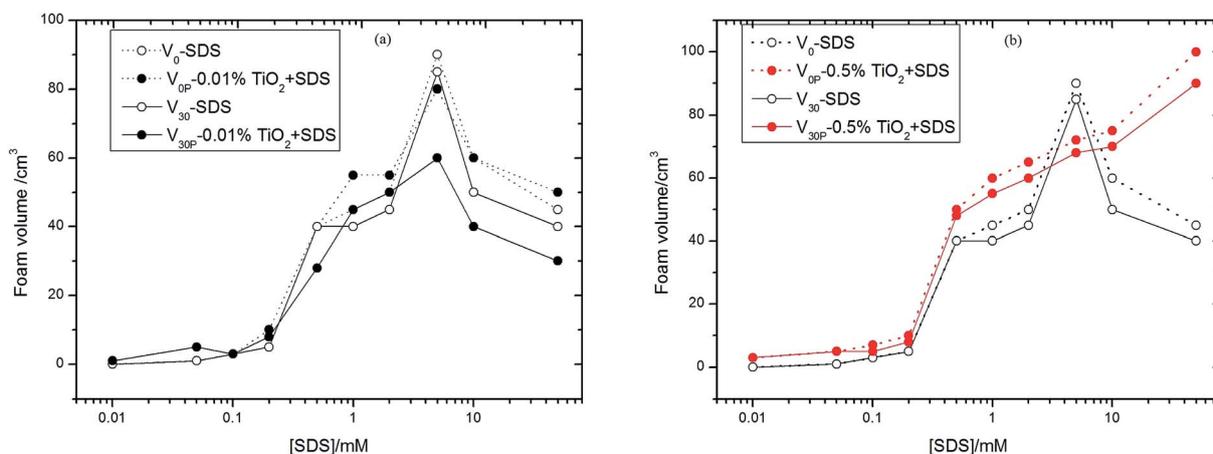

Fig. 2 Foam volumes without and with TiO_2 particles were shown at different SDS concentration. (a) Particle concentration of 0.01%, where the standard deviations for V_0, V_{30}, V_{0P} and V_{30P} were ± 2.8 cm^3, ± 2.8 cm^3, 2.5 cm^3, and ± 2.0 cm^3, respectively. (b) Particle concentration of 0.5%, where the standard deviations for V_{0P} and V_{30P} were each ± 3.0 cm^3.
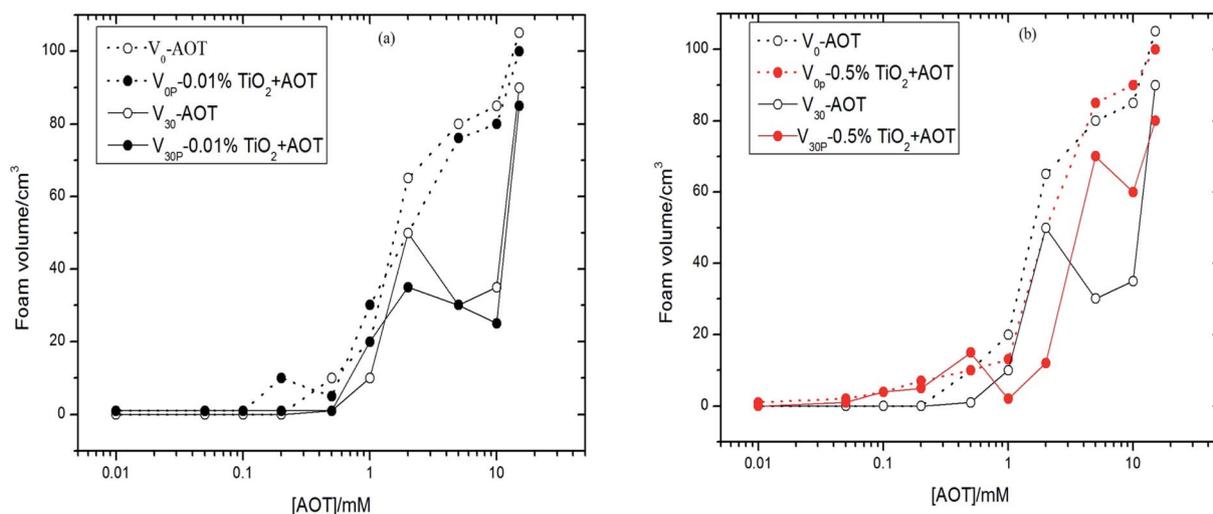

Fig. 3 Foam volumes without and with TiO_2 particles were shown at different AOT concentration. (a) Particle concentration of 0.01%, where the standard deviations for V_0, V_{30}, V_{0P} and V_{30P} were ± 3.2 cm^3, ± 2.3 cm^3, ± 3.1 cm^3, and ± 2.2 cm^3, respectively. (b) Particle concentration of 0.5%, where the standard deviations V_{0P} was ± 3.0 cm^3 and that of V_{30P} was ± 2.6 cm^3.
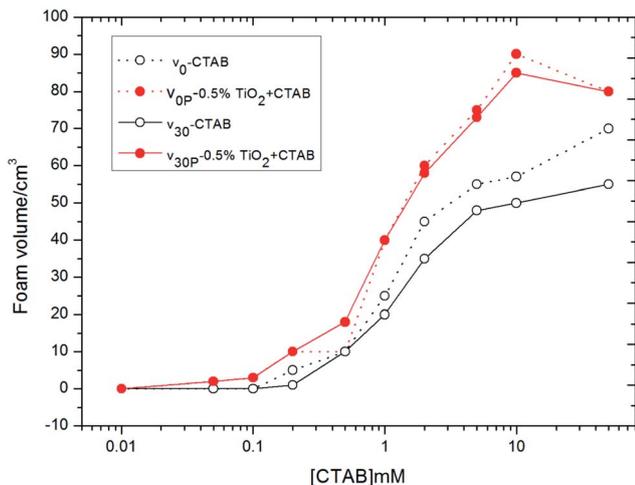
Fig. 4 Foam volumes without and with TiO_2 particles were shown at different CTAB concentration. Particle concentration was 0.5%, where the standard deviations for V_0, V_{30}, V_{0P}, and V_{30P} were ±2.5 cm³, ±2.4 cm³, ±2.8 cm³, and ±2.8 cm³, respectively.

0.01%, foam volumes of V_{0P} and V_0, as well as V_{30P} and V_{30}, showed similar trends. Beyond 8 mM, the foam volumes of V_{30P} were less than those of V_{30}. However, for higher particle concentration of 0.5% (see Fig. 2b), the curves of V_{0P} and V_{30P} monotonously increased with the increase of SDS concentration, which was obviously different from the corresponding curves of 0.01% particle concentration. The V_{0P} and V_{30P} values were larger than V_0 and V_{30} values in the entire range of surfactant concentrations, except near the CMC of SDS, where the values of V_0 and V_{30} were the highest. Thus, we initially inferred that TiO_2 particles can affect foamability and foam stability in SDS aqueous solutions and this influence was strengthened as particle concentration increased. The curves of V_0 and V_{30}, as well as those of V_{0P} and V_{30P}, almost overlapped in Fig. 2b, which denoted the systems of SDS-aqueous solution

without and with TiO_2 particles both had strong foam stabilities in water.

The four foam volumes were also measured with 0.01% and 0.5% of TiO_2 particles dispersed in AOT-aqueous solution at different AOT concentrations compared with AOT alone, as shown in Fig. 3. The value of AOT alone (V_0) increased with the increase of AOT concentration, while the value of AOT alone (V_{30}) showed three phases, $i.e.$, going up with the increase of AOT concentration from 1 mM to 2 mM, rapidly falling from 2 mM to 5 mM, then quickly rising again above 5 mM. And the CMC of AOT in pure water is just near 2 mM.[32] With 0.01% of TiO_2 particles dispersed AOT-aqueous solutions, the values of V_{0P} and V_{30P} showed similar changes as those observed for the corresponding V_0 and V_{30} values, and the values of V_{30} and V_{30P} were generally smaller than those of V_0 and V_{30}, which was similar to that observed for the TiO_2–SDS mixed aqueous solutions. When particle concentration was increased to 0.5%, the values of V_{0P} and V_{30P} were still no larger than those of V_0 and V_{30}, except from 5 mM to 10 mM where V_{30P} was beyond V_{30}, which were obviously different from those of TiO_2–SDS solution at same particle concentration of 0.5%. Therefore, it was indicated that TiO_2 particles did not provide a strong active effect on foamablity and foam stability as a whole in AOT aqueous solutions.

Considering the influence of the low particle concentration of 0.01% on the foam volumes above, V_{0P} and V_{30P} were measured only with 0.5% of TiO_2 particles dispersed in aqueous solutions of CTAB, and the results were given in Fig. 4. The values of V_0 steadily increased with increasing CTAB concentrations, where the minimum concentration of CTAB is required to stabilize foams approached 0.9 mM, which is its CMC in water.[33] When TiO_2 particles were added into CTAB aqueous solutions, the values of V_{0P} and V_{30P} presented remarkable increases beyond the CMC, which were much higher than the values of V_0 and V_{30} in the whole range of CTAB concentration, although the values slightly decreased above
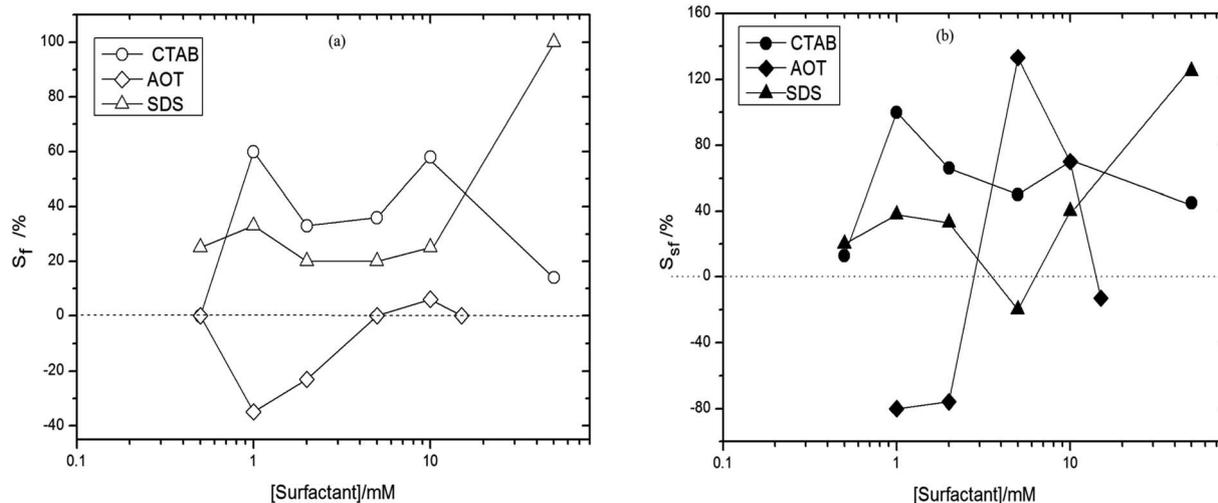

Fig. 5 Effect of surfactant concentration on (a) S_f (foamability) and (b) S_{sf} (foam stability), calculated using the data in Fig. 2b, 3b and 4, for TiO_2 particle plus SDS, AOT and CTAB systems, respectively.

10 mM. Similar to the foam volumes of the mixed system of SDS plus TiO_2 in Fig. 2b (0.5% of TiO_2), the curves of V_{0P} and V_{30P} almost overlapped, implying that TiO_2 particles, with the participation of CTAB, provided an excellent stabilizing effect on the foam at the air–water interface.

Using $S_f\% = (V_{0P} - V_0) \times 100\%/V_0$ to denote the degrees of foamability (shaken immediately with surfactant alone (V_0) and surfactant plus TiO_2 particles (V_{0P})) and $S_{sf}\% = (V_{30P} - V_{30}) \times 100\%$ to denote foam stability (shaken after 30 min with surfactant alone (V_{30}) and surfactant plus TiO_2 particles (V_{30P})), we further studied the effect of interaction of TiO_2 particles with surfactants on the foamability and foam stability in aqueous solutions. The values of S_f and S_{sf} above zero indicated the interaction of particles with surfactants was synergistic, otherwise the interaction was antagonistic. The relations of S_f and S_{sf} with surfactant concentration were shown in Fig. 5, where the data used to calculate S_f and S_{sf} were from Fig. 2b, 3b and 4. The S_f and S_{sf} values for TiO_2–CTAB were higher than those for
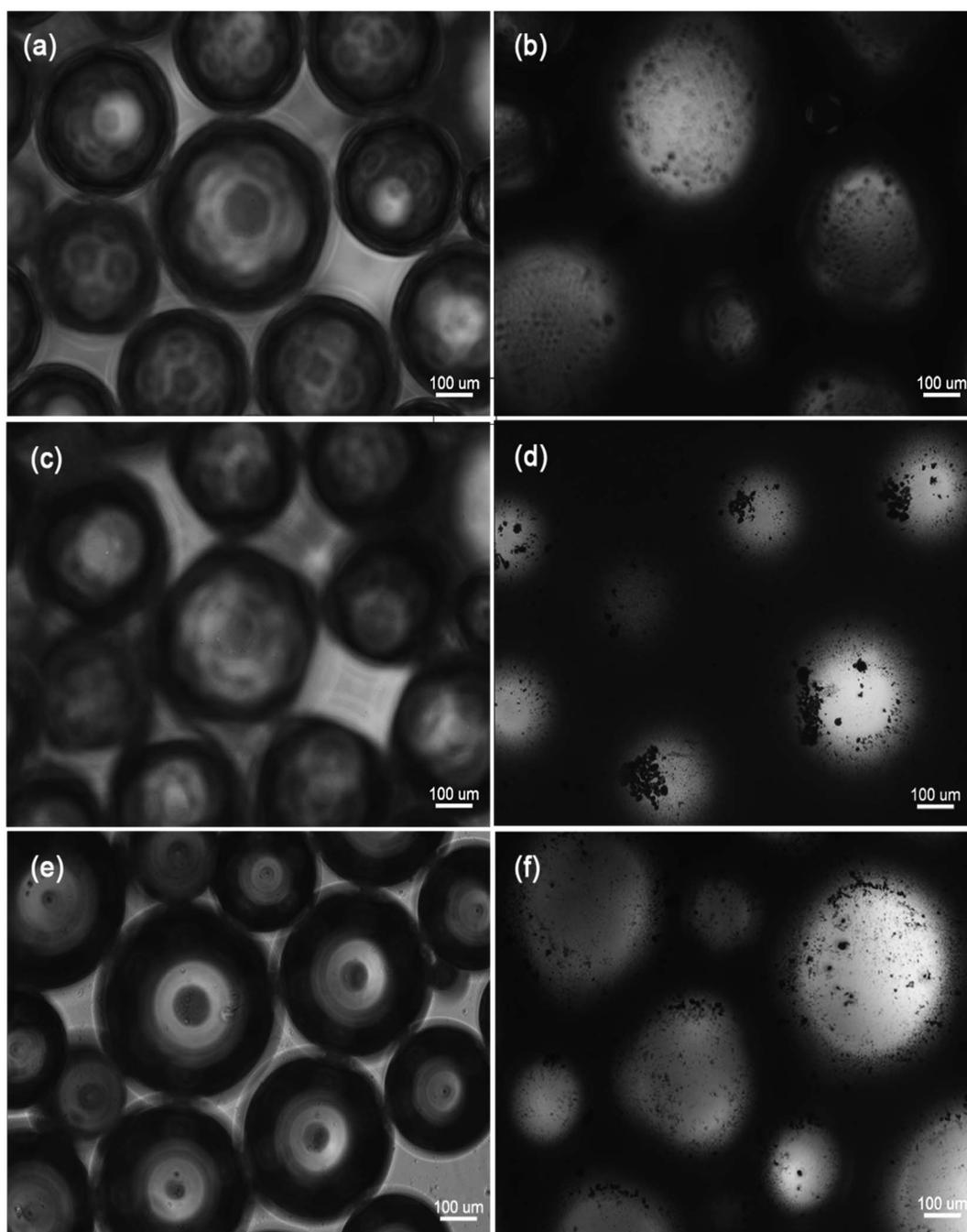

Fig. 6 Optical micrographs of foams were stabilized by surfactant alone and by a mixture of TiO_2 particles and surfactant, taken 30 min after aeration. The first set: (a) 1 mM SDS and (b) 0.5 wt% TiO_2 + 1 mM SDS. The second set: (c) 5 mM AOT and (d) 0.5 wt% TiO_2 + 5 mM AOT. The third set: (e) 10 mM CTAB and (f) 0.5 wt% TiO_2 + 10 mM CTAB.

TiO$_2$–SDS from 0.5 mM to 10 mM; however, this was reversed when surfactant concentration was beyond 10 mM. Therefore, the synergistic effects of TiO$_2$ and CTAB were stronger than those of TiO$_2$ and SDS at moderately higher surfactant concentrations.

Discussion

For the SDS–TiO$_2$ mixed aqueous solution (Fig. 2b), foam volumes for SDS alone were small at surfactant concentrations below 0.2 mM, the cause of which may be fewer free surfactant molecules that would be unable to form a sufficiently dense network at the air–water interface surrounding the bubbles to prevent coalescence. With the increase of surfactant molecules, the curves of V_0 and V_{30} presented *para*-curve with the maximum values near the CMC of 8 mM. The ascending part of the curves was due to the presence of more surfactant molecules that spread a dense layer at air–water interface to prevent the drainage between bubbles, and the descending of the curves was linked to the increase in the lifetime of the micelles with concentration, leading to the reduction of the supply of monomeric SDS molecules required for the stabilization of the fresh bubble at the interfaces.[34,35] As was observed, at low concentrations, *i.e.*, from 0.2 mM to 0.5 mM, the foam stabilization mainly depended on SDS molecules and TiO$_2$ particles only had a slight effect on foams. Beyond 0.5 mM, the values of V_{0P} and V_{30P} were obviously larger than those of V_0 and V_{30} (excluding those values near the CMC of SDS) at the same concentration, the improvement of which just came from the synergistic effect between SDS molecules and TiO$_2$ particles. The hydrophilic headgroups of SDS molecules were adsorbed onto the surfaces of TiO$_2$ particles and hydrophobic carbochains were directed toward air during the interaction, rendering the surfaces more hydrophobic, and thus they were adsorbed easily onto the surfaces of foams as shown in Fig. 6b. Therefore, the V_{0P} and V_{30P} curves nearly monotonously ascended with the increase of SDS concentration in Fig. 2b.

As for the AOT–TiO$_2$ mixed system (Fig. 3b), the values of V_0 monotonously increased from 1 mM and were higher than the corresponding values for SDS in aqueous solution, which accounted for a double chain anion surfactant being more easier to aggregate at interface than its single chain analogues. Unlike the curves of SDS alone and CTAB alone (see Fig. 2b and 4), the foam curves of V_0 and V_{30} of AOT showed an abnormal fall of V_{30} in the range of 2 mM to 5 mM where was just the initial formation of AOT micelles,[32] which might be the cause for the decrease of V_{30}. However, at this concentration region, adding TiO$_2$ particles into AOT aqueous solution, it caused the value of V_{30P} to quickly increase, even exceeding that of V_{30}. Additionally, the value of S_{sf} near 5 mM reached a maximum value among the three mixed systems, which was certified in Fig. 6d where the number of particles adsorbed onto the surface of foam was significantly higher than that in Fig. 6b and f. Why did such a strong synergistic effect between TiO$_2$ and AOT in foam stability occur in the range of 2 mM to 5 mM? In relation to the abnormal fall in foam stability of AOT alone, we guessed that TiO$_2$ particles became so hydrophobic in this phase

because of the electrostatic interaction with AOT hemimicelles or quasimicelles. Because these hemimicelles or quasimicelles were not closed, their charged hydrophilic head groups would adsorb onto TiO$_2$ particles by electrostatic interaction with counter charges of the surface of TiO$_2$ particle, and bulky hydrophobic tails would extend to the interface, causing TiO$_2$ particles easily to adsorb onto the surface of the foam to prevent coalescence, which was described in Fig. 7. After AOT formed stable-closed micelles at AOT concentration above 5 mM, the hydrophilic head groups of the outer micelles lead to particles desorbing from the air–water interface.

Different from the interaction of CaCO$_3$ and CTAB, which was no synergistic effects in aqueous solution,[24] a strongly synergistic action occurred between TiO$_2$ and CTAB in both foamability and foam stability, as showed in Fig. 4 and 6f. The foam volume plus TiO$_2$ particles was much larger than that of CTAB alone above CMC (Fig. 4). And, the values of S_f and S_{sf} were all larger than zero in Fig. 5. Moreover, the foamability and foam stability of the TiO$_2$–CTAB mixed system were superior to those of the TiO$_2$–SDS mixed system in a wide range of surfactant concentration, *i.e.*, the surfaces of TiO$_2$ particles, due to the interaction with cationic CTAB surfactant, were more hydrophobic than those with anionic SDS surfactant. Besides, the surface of SiO$_2$ was also activated by CTAB in aqueous system, where the hydrophobicity of particles were enhanced by the adsorption of the hydrophilic headgroup of the molecule onto the particle surface while hydrophobic chain is directed towards interface.[21] When the concentration was above 10 mM, a second layer of surfactant gradually formed on the surface of TiO$_2$ particles by chain–chain interactions with the first layer of molecules, which reduced the hydrophobicity of TiO$_2$. Therefore, the values of V_{0P} and V_{30P} for the TiO$_2$–CTAB mixed system began to decline with the increase of surfactant concentration from 10 mM. Contrastively, the foam values of V_{0P} and V_{30P} of
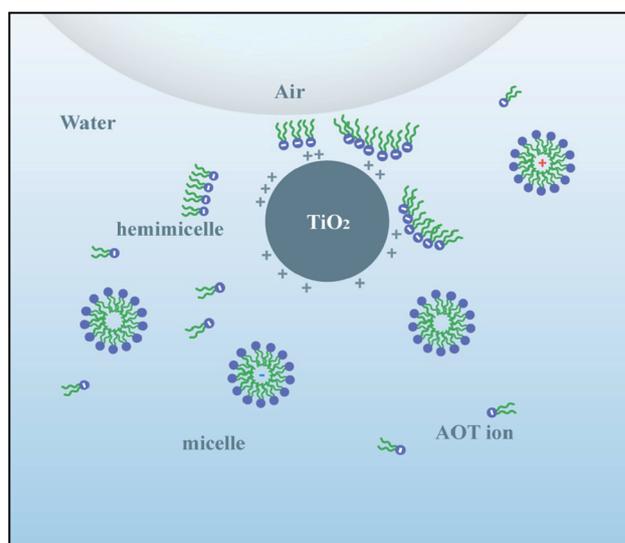

Fig. 7 Schematic representation of the likely cause was responsible for the strengthening synergistic effect between TiO$_2$ and AOT in foam stability in the region of 2 mM to 5 mM of AOT concentration, where TiO$_2$ particles were easily adsorbed onto the surface of foam.

the TiO$_2$–SDS mixed system monotonously increased with the increase of SDS concentration, implying that only a single layer of surfactant molecules was adsorbed onto the surface of TiO$_2$ particles, even at higher SDS surfactant concentrations.

Conclusion

The synergistic effects of TiO$_2$ particles with surfactants SDS, AOT, and CTAB were studied by measuring foam volumes in aqueous solutions with surfactant alone and surfactant-TiO$_2$ mixed systems, calculating the degrees of the foamability S_f and foam stability S_{sf}, and observing the adsorption of activated TiO$_2$ particles on the surface of foams using optical micrographs. The results indicated the interaction between TiO$_2$ and SDS, as well as that between TiO$_2$ and CTAB, was significantly synergistic above the surfactant concentration of 0.5 mM; the effect of TiO$_2$ and AOT was only synergistic in foam stability near the CMC of AOT, and asynergistic in both foamability and foam stability at other concentrations. The system of TiO$_2$ and CTAB generally provided more synergistic effects than that of TiO$_2$ and SDS. However, the strongest synergistic effect occurred between TiO$_2$ and AOT near the concentration of 5 mM. AOT hemimicelles or quasimicelles at the CMC likely accounted for this case. Though SDS and CTAB surfactants were all advantageous to enhance the hydrophobicity of the surfaces of TiO$_2$ particles during the interaction, SDS molecules may be adsorbed as a single layer onto the particle surfaces, and CTAB molecules maybe formed a bilayer to reduce the hydrophobicity of particle at higher concentrations.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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