Effect of colloidal particles on the foamability and stabilization of aqueous foams by cationic surfactant CTAB

Huiying Cao¹, Jiayi Chen¹, JieCai¹ and Yapin Li², ∗

¹School of Information and Engineering, Guangdong Medical University, Zhanjiang 524023, China
²School of Electrical Engineering and Automation, Jiangsu Normal University, Xuzhou 221116, China.

∗Corresponding author E-mail: pinyali@163.com

Abstract. Colloidal particles can influence the foamability and stabilization of aqueous foam by addition of surfactant at the air-water interface. This occurs because particles are activated via the interaction with surfactant and are adsorbed onto the surfaces of foams. This phenomenon has been applied extensively to the development of new materials and techniques. Whether particle surface can be activated or not is decided by the interaction between the surfactant and the particle. In this work, we studied the effects of cationic surfactant CTAB (cetyltrimethylammonium bromide) on PS (polystyrene), SiO₂, and TiO₂ particles in aqueous solution, and compared the difference in their surface activation according to foam volume of the particles/CTAB/water system, and the degrees of foamability and foam stabilization. In addition, the influence of anionic surfactant SDS (sodium dodecyl sulfate) on the surface activation of PS in aqueous solution was also analyzed and compared with that of CTAB.

1. Introduction

Colloidal particles can be strongly attached to liquid–vapor interface by the activation of their surfaces, behaving as foam stabilizers [1-2]. Foams coated with sufficient particles will keep long-term stability under quiescent conditions because the adsorption of particle onto the foam surface is irreversible, which is different from the adsorption and desorption of surfactant molecules on a rapid timescale. Therefore, many new significant technologies have been emerged based on this phenomenon, such as, liquid marbles (large liquid droplets encapsulated in air) [3-4], dry water (water in air powder) [5-6], colloidosomes [7], and anisotropic particles [8], which have been applied in food, cosmetics, medicine, and functional materials [9-10].

Small surface-activated particles, i.e., particles with higher adsorption free energy than the thermal energy, kT [11], can be obtained by various approaches, including the production of "Janus" particles with dual surface-functionality (half of the surface is hydrophilic and the other half is hydrophobic) [12-13], and the modification of the hydrophilic surface of particles with a homogeneous hydrophobic surface coating [14]. Unfortunately, these approaches are less practical due to inherent limitations. It is well known amphiphilic compounds can change the properties of particle surface in a solution. Surfactants, as common amphiphilic compounds with easy availability and low cost, can mediated the
activation of particles by adsorbing surfactant molecules onto particle surface in aqueous solution [15]. Therefore, adding surfactant into water to enhance the activation of particle surface is undoubtedly an effective strategy.

Surfactants added into water to activate particle surface have been successfully applied in many cases. In particular, the anionic surfactant SDS (sodium dodecyl sulfate), has been used to convert dry water into aqueous foam by changing the surface activation of silica particles in aqueous systems [16], to activate the inactive surfaces of CaCO$_3$ nanoparticles in water [17], and to control the aggregation of gold nanoparticles in aqueous films [18]. Nevertheless, studies on the activation of colloidal particle surfaces by cationic surfactants in aqueous solutions are relatively limited. Moreover, the investigations have been more focused on SiO$_2$ particles [19] than on other oxide particles and polymer particles. In this work, by measuring foam volume and calculating the degrees of the foamability and foam stability, we studied the effect of cationic surfactant CTAB (cetyltrimethylammonium bromide) on the surface activation of PS (Polystyrene), SiO$_2$, and TiO$_2$ particles in aqueous solution. Additionally, we compared the activation of PS particles by CTAB with that by SDS to further understand the effect of surfactant on the activation of polymer particles.

2. Materials and method

2.1. Materials

PS and SiO$_2$ particles with average diameters of 535 nm and 300 nm respectively were collected from the Department of Chemistry of Nanjing University and the Technical Institute of Physics and Chemistry, CAS. Particles were originally delivered as a dispersion in deionized water and required dehydration through a multistage solvent swap using ethanol as intermediate solvent, followed by drying in a vacuum drying oven at 30°C. Scanning electron microscopy (SEM, Quanta 200) images of dried aqueous dispersion of PS particles (Fig.1a) and SiO$_2$ particles (Fig.1b), showed particles did not agglomerate and the surfaces of particles were smooth and integrated. CTAB and SDS of 99% purity were from Shanghai Geneland Biotech Co., Ltd., China, and used as received. Deionized water with a resistivity of 18.2 MΩ cm at 25°C was from a deionized water machine (LDD-01, Ludao, Shanghai, China).

Figure 1. Scanning electron microscopy (SEM) images of a dried aqueous dispersion of PS particles (Fig.1a) with average diameter of 535 nm [20] and SiO$_2$ particles (Fig.1b) with average diameter of 300 nm.

Particles were no aggregation and the surfaces of particles were smooth and integrated.
2.2 Methods

2.1.1. Preparation of dispersions of aqueous surfactant without and with particles. A series of surfactant solutions with different concentrations of CTAB (0.01-50mM) were dispersed in deionized water. The dried particles (PS and SiO$_2$) were weighed and added into these aqueous surfactant solutions. These mixed solutions without or with particles were respectively sealed into 50 ml beaker and then dispersed using a constant temperature magnetic stirrer (85-2, Changzhou, China) at 2400 rpm for 2-5 min.

2.1.2. Preparation and measurement of aqueous foams, the dispersion of aqueous surfactant without 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 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 $V_{op}$, and that 30 min after shaking was as $V_{30p}$. $V_0$ and $V_{op}$ were considered as the measure of foamability of aqueous surfactant solution without and with particles, respectively. $V_{30}$ and $V_{30p}$ were considered the measure of foam stability of aqueous surfactant solution without and with particles, respectively. These experimental procedures were repeated three times.

3. Results and discussion

Figs. 2a-2d showed foam volumes as a function of surfactant concentration in aqueous solution. For the mixed PS/CTAB/water (Fig. 2a) system, the optimum PS particle concentration for foaming was 0.06% by the repeated tests. As shown in Fig.2a, the $V_0$ values steadily increase with increasing CTAB concentration, with the minimum CTAB concentration required to stabilize the foams approaching 0.9mM, which is its CMC in water [21]. When PS was added into the aqueous CTAB solution, the values of $V_{op}$ and $V_{30p}$ increased with CTAB concentration increasing and were obviously larger than those of $V_0$ and $V_{30}$ on the whole. This indicates that the PS particles via interaction with CTAB can enhance the foamability and foam stability of the system. PS, with the same particle concentration of 0.06%, was added to the SDS aqueous solution (Fig. 2b). Although the $V_{op}$ and $V_{30p}$ values were no smaller than the corresponding values of the PS/CTAB/water system (Fig. 2a), they were smaller than the $V_0$ and $V_{30}$ values below 5mM. This indicated that the interaction of PS and SDS in water hardly affected the foamability and foam stability for SDS concentrations from 0.01mM to 5mM. When the SDS concentrations were more than 5mM, $V_{op}$ and $V_{30p}$ were larger than $V_0$ and $V_{30}$, indicating that the PS particles in SDS aqueous system contributed to the foamability and foam stability at higher SDS concentrations. Therefore, the effect of cationic surfactant CTAB on the surface activation of PS in water was stronger than that of the anionic surfactant SDS.

For the mixed SiO$_2$/CTAB/water system (Fig.2c), the optimal particle concentration for foaming was 0.1%, as confirmed by the repeated tests. The values of $V_{op}$ and $V_{30p}$ also increased with the increase of CTAB concentration, similar to the case of PS/CTAB/water system (Fig. 2a); however, they were slightly greater than the $V_0$ and $V_{30}$ values, which indicated that the effect of CTAB on the surface activation of SiO$_2$ in water was insignificant. As for the mixed TiO$_2$/CTAB/water system (Fig.2d), the optimum particle concentration was found to be 0.5%, and the values of $V_{op}$ and $V_{30p}$ increased remarkably, similar to those of the PS/CTAB/water system. Above CMC, although the $V_{op}$ and $V_{30p}$ values slightly decreased above 10 mM CTAB concentration, they were far higher than the $V_0$ and $V_{30}$ values in the entire range of CTAB concentration (Fig. 2d). In contrast to the PS/CTAB/water system, the curves of $V_{op}$ and $V_{30p}$ of TiO$_2$/CTAB/water were almost overlapped, implying TiO$_2$ particles, in the participation of CTAB, had an excellent stabilizing effect on the foam at the air-water interface. Comparing the foam volumes of the three systems (Fig.2a, Fig.2c, and Fig.2d), it can be seen that the $V_{op}$ and $V_{30p}$ curves for PS showed a sharp increase at low CTAB
concentrations; that is, the values of $V_{0P}$ quickly increased from 0 cm$^3$ to 70 cm$^3$ in the range of 0.1mM to 0.5mM (Fig. 2a). In contrast, the $V_{0P}$ and $V_{30P}$ curves for SiO$_2$ and TiO$_2$ (Fig. 2c and Fig. 2d) gradually increased in this range. However, over 1mM CTAB concentration, an inverse trend was observed; that is, the curves for SiO$_2$ and TiO$_2$ quickly increased, while the curves for PS increased slowly.

![Figure 2](image-url)

**Figure 2.** Foam volumes without and with particles were shown at different CTAB concentration (a, c, and d) and SDS solutions (b).

(a) PS concentration was 0.06%, and the standard deviations for $V_0$, $V_{30}$, $V_{0P}$ and $V_{30P}$ were ±2.3, ±2.0, ±3.5, and ±2.5 cm$^3$, respectively. (b) PS concentration was 0.1%, and the standard deviations for $V_0$, $V_{30}$, $V_{0P}$ and $V_{30P}$ were ±3.1, ±3.0, ±3.0, and ±2.7cm$^3$, respectively. (c) SiO$_2$ concentration was 0.1%, and the standard deviations for $V_{0P}$ and $V_{30P}$ were ±2.2 and ±1.7cm$^3$. (d) TiO$_2$ concentration is 0.5% [22], and the standard deviations for $V_{0P}$ and $V_{30P}$ were each ±2.8cm$^3$.

As $S_f = (V_{0P} - V_0) \times 100\% / V_0$ denoting the degree of foamability and $S_{sf} = (V_{30P} - V_{30}) \times 100\% / V_{30}$ denoting foam stability, we further studied the effect CTAB surfactant on the activation of particles in foamability and foam stability in aqueous solution. The results were showed in Tab. 1 and Tab. 2, where the data used to calculate $S_f$ and $S_{sf}$ were derived from Fig. 2a, Fig. 2c, and Fig. 2d. The values of $S_f$ and $S_{sf}$ were all greater than zero, indicating that the surfaces of all the three particles were activated via the interaction with CTAB. In Tab. 1, the values of $S_f$ and $V_{0P}$ for PS have no obvious difference from those for TiO$_2$ above 1mM, while both of them were obviously higher than the values of $S_f$ for SiO$_2$ at the same surfactant concentration. Below 1mM CTAB concentration (0.1-1mM), the values of $S_f$ and $V_{0P}$ for PS were surprisingly high, with $S_f$ reaching 620% at 0.5mM, that is, foam volume after shaking was increased six to seven times from without PS particles to with PS particles. However, the values of $S_f$ and $V_{0P}$ for TiO$_2$ and SiO$_2$ were not as large at
the same low CTAB concentration. This indicated CTAB had a unusually strong synergistic action with polymer particle of PS in low concentration; however, this did not happen between CTAB and oxide particles in the same range of concentrations. When the CTAB concentration was beyond CMC, the synergistic action between CTAB and PS began to weakened obviously, but the action between CTAB and oxide particles did not presented a change like that. According to the degree of foamability (Sf) and foam volume (V0P) for the three mixed particles/CTAB/water systems, it can be found CTAB exhibited the strongest activation effect on PS in aqueous solution, followed on the TiO2, and the weakest activation effect on SiO2.

Table 1. Degree of foamability, Sf, and foam volume, V0P, for the three mixed particles/CTAB/water systems.

| CTAB conc. (mM) | 0.5  | 1   | 5   | 10  | 15  |
|-----------------|------|-----|-----|-----|-----|
| PS              | Sf   |     |     |     |     |
|                 | 62%  | 88% | 45% | 49% | 46% |
|                 | V0P (cm³) | 72  | 75  | 80  | 85  | 95  |
| TiO2            | Sf   |     |     |     |     |
|                 | 10%  | 60% | 55% | 58% | 47% |
|                 | V0P (cm³) | 11  | 40  | 75  | 90  | 88  |
| SiO2            | Sf   |     |     |     |     |
|                 | 80%  | 20% | 9%  | 30% | 18% |
|                 | V0P (cm³) | 18  | 43  | 60  | 75  | 77  |

Tab. 2 showed the degree of foam stability, Ssf, and the foam volumes, V30P, for the three different particles in CTAB aqueous solution. According to the data, the Ssf and V30P values for TiO2 were far greater than those for SiO2 and PS above 1mM CTAB concentration. Nevertheless, the maximal Ssf value was obtained from PS/CTAB/water system, with Ssf reaching 400% around 0.5mM. This means foam volume after shaking 30 min was increased four times with the assistance of PS by the activation; while the values of Ssf and V30P for TiO2 and SiO2 were far smaller than this value at the corresponding concentration. However, with the increase of CTAB concentration (beyond 1 mM), foam stability of PS/CTAB/water quickly decayed then levelled off, conversely, that of TiO2/CTAB/water system did not take place obviously change. In summary, above 1mM, the largest degree of foam stability and foam volume were obtained from the TiO2/CTAB/water system, followed from the PS/CTAB/water system; below 1mM, it was the PS/CTAB/water system for the largest degree of foam stability and foam volume, followed for the TiO2/CTAB/water system. As for the SiO2/CTAB/water system, it was the smallest degree of foam stability and foam volume in the entire range of concentration. Therefore, although SiO2 particles can be easily activated by the interaction with anionic surfactant SDS [5,18] and were used to form dry water, liquid marble in water, the synergistic effect between SiO2 and CTAB were weak in foaming and foam stability. In contrast, PS had stronger synergistic effect with cationic CTAB than with SDS on foaming and foam stability in aqueous solution (showed in Fig.2a and Fig.2b). For another oxide particle, TiO2, an excellent activation was exhibited in foamability and foam stability both by CTAB and by SDS [21].
4. Conclusion

Based on the experimental results and discussion, the following conclusions were drawn:

(1) The surface activation of particles can be estimated from foamability and foam stability of the mixed particles/CTAB/water system. The cationic surfactant CTAB can all activate the surfaces of PS, SiO$_2$, and TiO$_2$ particles, of which were more activated in low CTAB concentrations than high concentration. Moreover, the foam stability and foam volumes first decreased and then levelled off with increasing CTAB concentration.

(2) Compared with the cationic surfactant CTAB, the anionic surfactant SDS adversely affected on the surface activation of PS colloidal particles in aqueous solution; however, this effect changed at higher SDS concentration.

(3) After activated by CTAB in aqueous solution, the strongest degree of foamability and the foam volumes ($V_{30P}$) were obtained from the PS/CTAB/water system, followed from the TiO$_2$/CTAB/ water system, and the weakest activation effect on SiO$_2$.

(4) After activated by CTAB in aqueous solution, the strongest degree of foam stability and the largest foam volumes ($V_{30P}$) were obtained from the TiO$_2$/CTAB/ water system above 1mM, followed fromthe PS/CTAB/water system, and the SiO$_2$/CTAB/ water was the worst; while below 1mM, the corresponding order became the PS/CTAB/water system, the TiO$_2$/CTAB/ water system, and the SiO$_2$/CTAB/water.

Overall, CTAB demonstrated the strongest activation effect on PS particle in aqueous solution, followed on TiO$_2$ particle, and the weakest effect on SiO$_2$.

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