Silica nanoparticles cationic surfactants interaction in water-oil system

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**HIGHLIGHTS**

- Interfacial behavior of CTAB-Silica nanoparticle complexes are measured and discussed at low surfactant/nanoparticle ratio.
- Dynamic IFT and elasticity measurements can shed light on the CTAB-Silica nanoparticle interaction and complexes.
- Standard deviation of drop shape from Laplacian form is a powerful tool for evaluation of complexes structure at interface.
- The initiation of closed-pack state can be detected by the standard deviation values more accurately.
- Nanoparticle-surfactants complexes show surface activity higher than similar surfactant solution, however slower kinetic.

**ABSTRACT**

The aim of this experimental study is to get insight into the combined interfacial and bulk properties of silica nanoparticles and CTAB cationic surfactant mixture in water/oil systems. The study is focused on low surfactant/nanoparticle ratios to avoid extra free surfactants in the bulk. Surfactant concentration was fixed at $9.0 \times 10^{-2}$ mM, (0.1 CMC) and the nanoparticle concentration varied between 0 and 5 wt.%. Drop profile analysis tensiometry (PAT) was utilized to measure the equilibrium and dynamic interfacial tension at water/heptane interface. To comprehend the layer structure of nanoparticle-surfactant complex at the interface, the interfacial rheology was also studied using drop oscillation experiments. The formation of the surfactant-nanoparticle complex layer at the drop surface and its different structures were explained using surface pressure vs. drop surface area curves and the standard deviations of experimental drop profiles from Young-Laplace equation during large compression/expansion cycles. The results demonstrate significant changes in the standard deviation at the onset of closed-packed state of surfactant-nanoparticle complex collapse. This illustrates the formation of irregular adsorbed layer (multilayer formation). The number of surfactant-nanoparticle complexes at drop surface was calculated...
1. Introduction

Surfactant-nanoparticle mixtures also known as complex fluid systems have been an important growing research area due to numerous technological applications. Particles in nano-scale have unique properties which stem from surface specifications of particle (forces, chemistry, shape and patterns) in this scale. We are seeking for any surface active agents (Surfactants, Proteins and Polymers, etc.) that can significantly improve their intrinsic properties and behaviors. These can be either a new enhanced property or the ability to control an unexpected behavior. To do so, we need to better understand surfactant-nanoparticles interactions in the bulk and at the interface. For example, the surfactant-nanoparticle complex can act as a novel surface-modifier agent and can be used for stabilizing dispersed systems, such as foams and emulsions. Furthermore, in many situations such as chemical EOR processes in petroleum industry or blood composition in drug delivery systems, the co-existence of surfactants and fine solid particles and therefore interaction between them is inevitable.

Generally, untreated nanoparticles such as hydrophilic silica are not surface active at liquid interface but their presence in a system containing surfactant can strongly affect the interfacial properties of the liquid [1]. They can influence surfactant surface activity or be surface-activated by adsorbing surfactants and modifying their hydrophilic/hydrophobic character. This has been observed in several studies for mixture of nanoparticle and surfactant, also for some cases that particles and surfactants were located in different phases [2–7]. It has been shown that a significant change in dynamics of adsorption and interfacial rheology can occur depending on the surfactant to nanoparticle ratio.

Some systematic studies on the mixture of silica nanoparticles and CTAB for water/air systems are available [8–14]. However, liquid-liquid systems are much less studied. In general, most of available works done in this field imply that there is a synergistic effect on the stability of foam/emulsions in the presence of nanoparticle. According to these results, adsorption of the particles at the interface is attributed to the electrostatic interaction between the negatively charged surface of the particles and the positively charged surfactants. The electrostatic interaction promotes the adsorption of the surfactant onto the particle surface and increases its hydrophobicity [14,15]. Ravera et al. [7,11–15] have extensively studied complex systems containing silica nanoparticle and CTAB. They found that the charged silica nanoparticles significantly reduce the effectiveness of the CTAB solutions at water-air and water-hexane interfaces. In their experiments the surfactant to nanoparticle ratio was very high. However, there are a few studies that show the silica nanoparticles can reduce surface tension of CTAB solutions at low or all surfactant concentrations [16,17].

It seems that this contradictory observation is due to the differences between the utilized surfactant to nanoparticle ratios that highly depend on the nanoparticle size and the surfactant and nanoparticle concentrations. At constant surfactant concentration, the surfactant to nanoparticle ratio is lower for smaller nanoparticles due to higher number of nanoparticles in the system. The aim of this study is to get insight into the combined effects of silica nanoparticles and CTAB on liquid/liquid interfacial properties at low surfactant to nanoparticle ratios. Therefore, we have performed various experiments on the system containing CTAB and silica nanoparticles with the size smaller than used in the most other works. The dynamic interfacial tension (IFT) values have been measured for different particle-surfactant compositions. In comparison with other pervious works in which the surfactant to nanoparticle ratios were mostly one order of magnitude higher than those used in the present work, only a few surfactants molecules adsorb at nanoparticles surface.

In addition to the dynamic interfacial tension, the response of the interfacial layer to low and high amplitude perturbations (interfacial area compression/expansion) can provide valuable information about the structure of layer of particles at liquid interfaces. At low amplitude surface area changes, the dilational visco-elasticity values can be measured. This can represent the reorganization of the mixed particle-surfactant complex layer [8,12,13,15,18]. However, the high amplitude surface area compression/expansion can also provide information about the interaction of particles and complexes at interface and add better understanding of the macroscopic structures of the particulate monolayers formed at the interface [12,19]. The traditional method of Langmuir film balance has been widely applied to obtain the surface pressure vs. surface area isotherms of particulate monolayers that consist of spherical nano- or micro-particles [20–24]. It has been observed that the composite system of nanoparticles and surfactant are able to form non regular solid structures at the water/air interface depending on the particles’ hydrophobicity and the presence of these structures influence the trends of isotherms for both compression/expansion path [3,12,25]. In the course of the surface compression, the adsorbed layer continuously reorganizes its structure until particles become closed-pack and form a solid-like structure. Further compression leads to the collapse of monolayer at a certain surface area at which the particles are pushed and wiped out of the interface and form a three-dimensional structure [26]. In certain cases, some useful parameters such as particle size, the force–distance curve for pairs of approaching particles and the three-phase contact angle of particle can be estimated by analyzing the data obtained from the surface pressure vs. surface area curves [27]. These calculations depend on the accurate assessment of the surface coverage at maximum packing of particles at the surface. This closed-pack state is usually detected through the knee in the surface pressure curve which can be estimated by determining the intersection point of the two tangents at the inflection points on its either side [24].

Most of the available works presenting nanoparticle structure at interface using surface area compression/expansion are performed via Langmuir Trough method considering surface tension measurements during surface area variation. Such results have been generally correlated with microscopic image observations. In this study, we have investigated the structure and collapse of the CTAB–Silica nanoparticle complex layer on the drop surface. We have used the PAT technique which is more accurate for measurement of dynamic surface/interfacial tension in such systems. In addition, the PAT technique applied in this research can also provide us the
standard deviations from the Laplace shape fitting which is introduced here as a better sensible and accurate parameter showing transition of a regular adsorbed layer to a complex film structure [28] during collapse of adsorbed layer.

2. Material and methods

In this study, various concentrations of aqueous silica particle dispersions in the presence of CTAB with constant concentration were prepared. The properties of the chemicals and preparing solutions and the experimental method and protocols are described in this section.

2.1. Chemicals

Levasil 300/30 (produced by H.C. Starck GmbH & Co. KG – Germany), a commercial colloidal dispersions of silica nanoparticles at 30.38 wt. %, was used as the source of nanofluid dispersion. Levasil 300/30 is free from any stabilizing additives and its high stability is obtained by a specific manufacturing process which uses the negative surface charge of the particles. Silica nanoparticles in the dispersion are spherical and monodispersed, with the average diameter around 9 nm and the specific BET area of 300 m²/g.

Hexadecyl trimethylammonium bromide (CTAB, Sigma, ≥99%) was used as cationic surfactant. Double distilled water was used as the aqueous phase and normal heptane was utilized as the oil phase. Heptane (liquid chromatography grade, purity ≥99.3%) was purchased from Merck and passed through a chromatographic alumina column three times to remove impurities.

2.2. Preparation of the surfactant-nanoparticle dispersion

Surfactant-nanoparticle dispersions were prepared by dilution of the nanoparticle source dispersion in two steps. In the first step, the initial dispersion was diluted to twice the target concentration by adding pure water. In the second step, an equal volume of the surfactant solution with double target concentration was added drop-by-drop to diluted dispersion. The whole dispersion was continuously stirred during this process to avoid particle aggregation in the course of dispersion preparation [15]. The final sample of the surfactant-nanoparticle dispersion was also sonicated in an ultrasonic bath.

2.3. Measurements

Measurements of dynamic interfacial tension and dilational visco-elasticity (elasticity, hereafter) at water-heptane interface were performed by a drop profile analysis tensiometer (PAT1, Sinterface Technology, Germany). Experimental set-up and principle of calculation were described elsewhere in detail [29]. Briefly, the process of measurement consists of image acquisition of drop profile, its digitalization and final fitting by the Gauss-Laplace equation. The pendant drop of aqueous dispersion was created at the tip of a stainless steel capillary by a computer driven dosing system in a glass cuvette filled with pure heptane. This fully computer controlled dosing system allows one to perform pre-programmed measurements with different protocol types such as dynamic interfacial tension measurements by keeping the drop volume/surface area constant. Moreover, the elasticity of interface layer can be measured by making sinusoidal perturbations in the surface area of the drop and analyzing the IFT response using a Fourier transformation program. In order to remain in the range of a linear perturbation response, the frequency range and the amplitude of these perturbations were between 0.01 and 0.1 Hz and 8% of the drop surface area, respectively [30,31]. In addition, in order to deepen the adsorption process of nanoparticles at the interface, the IFT changes and the deviation of the drop shape from its Laplacian shape were evaluated by applying large amplitude linear compression/expansion in the drop volume/surface area.

The dynamic foam ability of dispersions was measured by Bikerman method [32] in order to investigate the amount of the free surfactant in the system. The column was 50 cm high and 3 cm in diameter and the gas flow rates were between 2 and 10 ml/min. The used column was handmade and the porous plate was a sintered glass filter with pore size of 10–16 micrometer (VitraPOR®, Germany) that was suitable for air sparging.

All the experiments were conducted at 25 °C and atmospheric pressure. All glassware and Teflon equipment in contact with the liquid phases during sample preparation or measurements were cleaned by immersion in concentrated sulfuric acid followed by draining and rinsing copiously with distilled water. Before each measurement, the dynamic interfacial tension was measured for pure water/heptane interface to ensure the absence of any contaminants in the system. Each experiment was repeated at least three times to verify the reproducibility of the results and to eliminate the sources of uncertainty.

3. Results and discussion

3.1. Dynamic interfacial tension of nanoparticles without surfactant

The first set of experiments was conducted with nanoparticle dispersions without any surfactants. This reflects the pure effect of nanoparticles on the interfacial properties. Fig. 1 shows the dynamic interfacial tension of n-heptane/water in the presence of nanoparticles with different concentrations. As shown in the figure, the interfacial tension of the nanoparticle dispersion at all concentrations does not depend on drop surface age and the variation of interfacial tension is not significant. This result is consistent with the similar observations for air/water and hexane/water systems in the presence of untreated silica nanoparticles [27,10]. The silica nanoparticles are highly hydrophilic and have no tendency to adsorb at the interface. Therefore, nanoparticles do not stay at the surface, though they may reach the interface for a very short time, as a result of Brownian motion. These results also demonstrate negligible surface active contamination for both nanoparticle dispersion and the heptane phase.

3.2. Dynamic interfacial tension of surfactant-nanoparticle mixture

Dynamic interfacial tension of n-heptane/water containing constant CTAB concentration 9.0 × 10⁻⁴ m/M (0.1CMC) and different
nanoparticle concentration (0 to 2 wt.%) are presented in Fig. 2. As shown in this figure, when no nanoparticle exists in the system, the IFT is reduced quickly which means the surfactants reach to the drop surface in a short time. The diffusion of surfactant starts from the onset of drop formation in the cuvette and before the onset of measurements. However, the IFT starts at about 39 mN/m and approaches the equilibrium value within about 30 s. For the system containing nanoparticles, the IFT starts from values about 51 mN/m which is close to pure water/heptane IFT. This shows that the portion of free surfactant molecules in these systems is negligible and hence, they do not contribute to the initial rapid reduction of the IFT as we observed for pure surfactant system. Then, the IFT decreases gradually toward equilibrium value within much longer time (>1000 s, depends on nanoparticle concentration). It is more reduced by increasing the concentration of nanoparticle. This figure shows that the IFT of the mixture can decrease to the values lower than pure surfactant solution.

Hydrophilic nanoparticle, which has no tendency to adsorb at the interface, becomes partially hydrophobic due to adsorption of surfactants. This is attributed to the exposure of the hydrophobic tail of surfactant toward the aqueous bulk in the complex. Therefore, nanoparticles with higher hydrophobic property tend to adsorb at the interface. Since each nanoparticle carries a number of surfactant molecules, it acts as a surface active agent and the IFT is reduced due to the exchange of surfactant between nanoparticle and the interface. At the higher nanoparticle concentration, more number of surfactant-nanoparticle complex exist in the bulk which can adsorb to interface and hence the lower IFT is obtained at equilibrium condition. The size of individual nanoparticle-surfactant complex is much greater than the size of surfactant molecule and hence the diffusion coefficient of nanoparticle complex is lower. Nanoparticle complex needs a very long time to reach the interface and reducing the IFT in comparison to surfactant molecule.

3.3. Elasticity measurements

Fig. 3 shows IFT variations during regular low amplitude (about 8% of initial drop surface area) sinusoidal oscillation and linear path after equilibrium for two systems: pure CTAB and CTAB with 2 wt.% nanoparticle. It is evident that with similar surface/volume changes in two systems, the IFT variation for the second system (2.0 mN/m) is greater than that for the first system (0.4 mN/m). In the other words, in the absence of nanoparticle, the response of the system to the surface/volume changes is faster. This is attributed to the faster adsorption/desorption of small surfactant molecules in comparison to large complex of surfactant-nanoparticles to keep close to the equilibrium state.

The IFT variations during drop surface oscillation can provide modulus of the surface elasticity (E = A/δA). The calculated elasticity values of studied systems are shown in Fig. 4. The results illustrate very low elasticity values close to zero (region (1)) for nanoparticle solutions, close to pure water condition. This is an expected result according to negligible effects of pure silica nanoparticles on interfacial tension values. For pure surfactant solutions (without any silica particle), the elasticity values are between 5 and 10 mN/m (region (2)) depend on the applied frequency. However, for the mixture of surfactant-nanoparticle solutions, the elasticity values are much larger and in the range of 20–30 mN/m (region (3)) depend on the concentration of nanoparticle and applied frequency. It is observed that the lowest amount of added nanoparticles (0.5 wt.%) increase the elasticity significantly while addition of more nanopar-
particles results in a gradual increase in the elasticity. These results also indicate the presence of large complexes of nanoparticle-surfactant at the interface that can cause high elasticity values.

As mentioned before, complexes with higher hydrophobic property tend to adsorb at the interface. At the higher nanoparticle concentration higher numbers of complexes exist in the bulk, however with a bit lower surface activity due to decrease in surfactant to nanoparticle ratio. The size of nanoparticle-surfactant complexes is much larger than the size of surfactant molecule and hence the diffusion coefficient of nanoparticle complex is lower. This is also the main reason of high elasticity values for the mixture.

3.4. Large amplitude compression/expansion experiments

To get insight into the adsorption process of nanoparticle surfactant complexes at the interface, extra experiments were conducted at large amplitudes. The same pendant drop experiments were performed and the system was allowed to reach the equilibrium IFT. Then, the drop volume was undergone to a linear high amplitude (about 70% of initial drop surface area) compression and expansion at a rate of $2.0 \times 10^{-5}$ ml s$^{-1}$ and the IFT changes was evaluated in the course of this process.

Fig. 5 shows drop volume changes during this compression/expansion protocol along with the IFT response for the system with surfactant. The surface pressure evolution, IT (IFT difference from equilibrium condition), standard deviation from Laplacian shape fitting and images of drop during this experiment are shown in Fig. 6. The horizontal axis of this figure shows the normalized surface area of droplet respect to its initial value.

As shown in Fig. 6, the surface pressure changes slightly for CTAB layer, even for very high surface area compression of 70%, due to fast desorption process expected for regular surfactants. By increasing the drop surface area to its initial state, there is a hysteresis in the surface pressure curve. This can be related to difference in the kinetics of adsorption/desorption processes. Our results show if we keep the system intact after this compression/expansion and continue measuring, the surface pressure returns to its initial equilibrium value within less than 100 s (not shown here). This illustrates a reversible process. Further, we performed standard compres-

![Fig. 5. High amplitude drop volume compression/expansion protocol and the IFT response for CTAB solution at 9.0 × 10⁻² mM.](image)

![Fig. 6. Surface pressure and standard deviation changes during drop compression/expansion for CTAB solution (9.0 × 10⁻² mM). Initial drop volume: 20 mm³](image)
until the surface ratio of 0.42 and then it is increased sharply, afterwards. The images of the drop during the compression also show starting wrinkles on the drop surface after the surface ratio of 0.42 and at minimum surface area illustrate a hard-structure like membrane (Fig. 7).

To better understand this process, Fig. 8 schematically shows the structure of the adsorbed layer of nanoparticles during drop compression. When compression is in its early stages nanoparticle-surfactant complexes exist at the interface but they do not fully cover the drop surface (Fig. 8a). After onset of compression, surfactant-nanoparticle complexes become closer to each other and as a result, the ratio of the complex number to drop surface increases. In this case the surfactants cannot be removed from the interface because of the strong bonds with nanoparticles and thus the IFT decreases (surface pressure increases) linearly and more than when there is no nanoparticle in the system. The non-linear rise in the surface pressure before the plateau region can be related to the long-range repulsive interaction between nanoparticles according to Aveyard et al. [33] (Fig. 8b).

With further compression in a certain surface ratio, i.e. 0.45, surfactant-nanoparticle complexes fully cover the surface and create a solid-like membrane which is deformed significantly against further compression (Fig. 8c). Therefore, the shape of drop deviates from the Laplacian form and hence the standard deviation starts to increase intensely. As shown in Fig. 7, the rise in the standard deviation curve starts at the surface ratio that the surface pressure curve has the inflation point. According to the conventional studies using the Langmuir film balance, this inflation point indicates the closed-pack state of nanoparticles at the surface.

When the surface is fully covered by nanoparticle complex and more compression occurs, some rearrangements in the special position of the complexes such as surface folding or expelling particles from the surface can occurs to compensate this compression [33] (Fig. 8d). Therefore, the rate of surface pressure increase can fall and the surface pressure becomes constant between surface ratios of 0.44 and 0.42.

With further surface ratio reduction below 0.42, the standard deviation increases steeply. It seems that at this point, the monolayer formed on the drop surface loses its resistance against further compression and breaks (Fig. 8e). The wrinkles on the drop surface shown in the images of Fig. 7 are formed due to this phenomenon. It should be noted that beyond the surface collapse and the sharp rise in standard deviation, all the measured interfacial tension with a non-Laplacian drop shape have to be treated with caution to avoid misleading. Therefore, in addition to the interfacial tension variations, the standard deviation values (from Laplacian shape fitting) can be an excellent parameter for indication of closed-pack state of nanoparticles and monolayer collapse afterwards. The importance of this parameter has been also discussed for alkane vapor adsorption on surfactant solution drop at the last stages that liquid lens film formation can occur [28].

3.5. Elasticity measurements during large compression path

In a similar experiment for this system, the viscoelasticity parameters at different stages of drop compression are measured by performing simultaneous regular amplitude (8% of drop surface area) sinusoidal perturbations. Fig. 9 shows the drop volume and the measured interfacial tension during a continuous large drop surface compression for CTAB solution (9.0 × 10⁻² mM) with 1 wt% nanoparticle. Points E.1 to E.4 indicate the positions which the visco-elasticity coefficient were measured (displayed values on the graph). As shown in this figure, the elasticity measurements were performed firstly just before the onset of drop compression (E1 point). At this point the elasticity is about 25.0 mN/m which is in a similar range of measured values for the same system in Fig. 4 (CTAB & 1 wt.% np at f = 0.02 Hz) before compression. The second elasticity measurement was performed at drop volume of about 16 mm³ for which the surface pressure still rises linearly (E2 point). The results show that despite the relative increase in the concentration of nanoparticles at the surface, the elasticity has not changed significantly (25.1 mN/m) and is almost equal to that before the drop was compressed. The point E.3 displays the third elasticity measurement at drop volume around 8 mm³ after the region of non-linear increase of the surface pressure before the
closed-pack state of nanoparticles monolayer. Significant increase in elasticity values up to about 41.5 mN/m is related to onset of complexes interaction at the drop surface. The last elasticity measurement region at the drop volume about 4 mm³ (after collapse region) shows the elasticity about 17.5 mN/m which is unexpectedly low. Moreover, nonlinear behavior (anomalous response) was observed in IFT response to the changes in the interfacial area. As previously mentioned, the drop adopts non-Laplacian shapes in this region and the calculated values as interfacial tension represents an apparent membrane tension with a certain error. Therefore the high values of standard deviation from Laplacian shape fitting still show an abnormal fragmented membrane-like layer.

### 3.6. Estimation of nanoparticle quantity at interface

For many fundamental and technological applications, it is always an important question to estimate the quantity of nanoparticles at the interface. There are several approaches trying to provide such important estimations, which are mostly based on high resolution image analysis and observation of the particles at the interface, chemical composition analysis or interaction force techniques. In this research in addition to surface pressure measurements, elasticity value and standard deviations from Laplacian shape fitting are used for quantifying nanoparticles at interface. Both parameters can be considered as more sensible indication than surface pressure for particle/complex interaction forces at the interface. Fig. 10 shows the surface pressure changes and the standard deviation values from Laplacian shape fitting for different nanoparticle concentrations. These results illustrate that the closed-pack state (red points in the surface pressure and standard deviation curves) and the surface collapse occur earlier with increasing nanoparticle concentration. In addition, the rate of increases in the surface pressure before the collapse is also larger for higher nanoparticle concentrations and the surface pressure variations deviate from the linear trend earlier. The images of drops at maximum surface compression for all systems are also shown in the inset of Fig. 10b. It is clear that at higher nanoparticle concentrations, the drop is skewed more and deviate further from its Laplacian shape and more wrinkles appears on the surface. This is due to more adsorption of nanoparticle surfactant complexes at the interface that causes shorter distance between them that result in faster and stronger interactions during compression.

The surface area ratio at closed-pack state of nanoparticles is also shown in Fig. 10a. Estimation of drop surface area at closed-pack state by mentioned procedure can provide us the number of surfactant-nanoparticle complexes at the surface. It was assumed a 2-D hexagonal structure for nanoparticles monolayer with packing density of 0.91 [34,35]. As shown in Table 1, the number of complexes increase from $1.87 \times 10^{11}$ to $2.93 \times 10^{11}$ (1.5 times) with a fourfold rise in the nanoparticle concentration from 0.5 to 2.0 wt.%. Considering the nanoparticle size ($d = 9$ nm) and density ($2.4$ gr m$^3$) and also the concentrations of surfactant and nanoparticle, the number of surfactant and nanoparticle and hence the bulk surfactant/nanoparticle ratio can be obtained for each system. Further, we assumed that there is no free surfactant in the bulk (it will be discussed in the followings). Accordingly, the average number of the surfactants adsorbed at each nanoparticle surface varies between 2 and 11 depending on the nanoparticle concentrations.

The lack of free surfactant in this systems can be asserted from the results of Ravera et al. [7] that studied the surfactant-nanoparticle mixtures with higher nanoparticle size (15 nm). According to their work while the initial CTAB concentration was $8.0 \times 10^{-2}$ M, for nanoparticle concentrations larger than 0.4 wt.% there was no free surfactant available in the bulk. It means that when the surfactant to nanoparticle ratio is less than 510, surfactants are completely depleted from the bulk to nanoparticles surface. In the other words, the maximum surface area on the nanoparticle surface occupied by surfactant is about 1.4 nm². The nanoparticles in this study have similar surface properties as those in Ravera et al., but they have the smaller size and hence the lower surface area per nanoparticle. Applying this value for the present nanoparticles, the minimum required number of surfactant molecule per nanoparticle to expect free surfactant in the bulk is about 183. This number is much higher (16–66 times) than the surfactant to nanoparticle ratios in this study and ensures the lack of free surfactant in the bulk.
Table 1
Calculated number of substances in bulk and interface for all investigated systems

<table>
<thead>
<tr>
<th>Nanoparticle Concentration wt.%</th>
<th>Overall Nanoparticle Number</th>
<th>Surfactant to Nanoparticle Ratio</th>
<th>Drop Area at Closed-pack mm²</th>
<th>Interface Complex Number</th>
<th>Interface Surfactant Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.41 × 10¹³</td>
</tr>
<tr>
<td>0.5</td>
<td>1.09 × 10¹⁴</td>
<td>11.03</td>
<td>13.09</td>
<td>1.87 × 10¹¹</td>
<td>8.79 × 10¹¹</td>
</tr>
<tr>
<td>1.0</td>
<td>2.18 × 10¹⁴</td>
<td>5.51</td>
<td>15.32</td>
<td>2.19 × 10¹¹</td>
<td>1.21 × 10¹²</td>
</tr>
<tr>
<td>1.5</td>
<td>3.27 × 10¹⁴</td>
<td>3.68</td>
<td>16.70</td>
<td>2.39 × 10¹¹</td>
<td>8.79 × 10¹¹</td>
</tr>
<tr>
<td>2.0</td>
<td>4.37 × 10¹⁴</td>
<td>2.76</td>
<td>20.49</td>
<td>2.93 × 10¹¹</td>
<td>8.09 × 10¹¹</td>
</tr>
</tbody>
</table>

*Surfactant numbers for all solutions is 1.20 × 10¹⁵ (for CTAB concentration 9.0 × 10⁻² mM).

Fig. 11. Equilibrium interfacial tension vs. CTAB concentration and the adsorption isotherm parameters for the best fit of Langmuir model.

Fig. 12. Empty point: calculated number of surfactant-nanoparticle complexes and surfactants associated with complexes at the interface vs. nanoparticle concentration. Filled points: the measured interfacial tension and elasticity of surface at equilibrium condition. The lines are drawn to guide the eyes.

Therefore, the number of surfactants associated with nanoparticles at the interface can be estimated as shown in the Table. 1. It decreases from 2.07 × 10¹² to 8.09 × 10¹¹ as the nanoparticle concentration increases from 0.5 to 2.0%. For a better comparison, the number of surfactant molecules at the interface in the absence of nanoparticles was also calculated and is shown in Table 1. For this aim, the Langmuir isotherm was used to fit the equilibrium interfacial tensions vs. CTAB concentration and the surface coverage was obtained according to the adsorption model parameters that is shown in Fig. 11 along with the experimental data.

According to these results, about 7.41 × 10¹³ surfactant molecules are at the surface at equilibrium condition which at least one order of magnitude more than the number of surfactant adsorbed at surface along with nanoparticles. However, in the presence of nanoparticles the equilibrium interfacial tension is more reduced despite the slow process of adsorption. Fig. 12 is presented here to better understand the impact of the presence of nanoparticles on surface activity of the system. This figure shows the equilibrium interfacial tension and the surface elasticity of the system based on surfactant-nanoparticle complexes and the number of surfactants associated with these complexes vs. nanoparticle concentration. The number of complexes at the interface increases with increasing nanoparticle concentration, although the surfactant to nanoparticle ratio is decreased and complexes might be less surface-active. However, these complexes even with low number of attached surfactants, are still enough surface-active to be adsorbed at the interface. Therefore, for the range of concentrations used for surfactant and nanoparticles, the hydrophobicity of nanoparticles does not change dramatically and the complexes concentration has a greater impact on reducing IFT. However, dynamic interfacial tension variations are much slower in comparison to surfactant solutions due to much smaller diffusion coefficients. This is more discussed in the next section describing foamsability experiments.

3.7. Foamsability experiments

To confirm the absence of free surfactants in the composite systems in this study, the dynamic foamsability of the dispersions were investigated. The results shows that none of the surfactant-nanoparticle dispersion had foamsability in contrast to the systems containing pure surfactant which enable to establish foam even at much lower surfactant concentration (Fig. 13). In this experiment the bubble formation and its contact with aqueous phase occurs at very short time which can be less than one second. Therefore, it can be concluded that very low foamsability of the system in presence of nanoparticle is related to the absence of free surfactants in system and insufficient time for adsorption of surfactant-nanoparticle complex to the bubble surface. The absence of free surfactant was also shown based on the results of Ravera et al. [7] in previous sections.

4. Conclusions

Different experimental protocols based on profile analysis tensiometry were applied for investigation of CTAB and hydrophilic silica nanoparticle solutions at low surfactant to nanoparticle ratios in which only a few surfactant molecules adsorb at nanoparticles surface. The dynamic interfacial tension was measured as a function of nanoparticle concentration. In addition, the response of the interfacial layer to low amplitude surface area perturbations and large compression/expansion were measured that provide valuable information about the behavior of surfactant-nanoparticle complex monolayer at the drop surfaces. The following conclusions can be drawn based on the results obtained in this study:

Hydrophilic silica nanoparticles are not surface active alone and have no significant effect on water/heptane interfacial tension and visco-elasticity values in the range of studied concentration (0.1–5%). In the presence of CTAB, nanoparticles become surface active complexes by adsorbing surfactant molecules and strongly affect the interfacial properties. The systems containing both surfactant and nanoparticles illustrate lower equilibrium IFT and it is more reduced with increasing the concentration of nanoparticle. However, the dynamics of the IFT reduction is much slower than CTAB solutions without nanoparticle. In the presence of nanoparticle, the visco-elasticity of the interface is much higher in the range
of applied frequency, and increases slightly with increasing concentration of nanoparticle. This is expected due to much bigger size of nanoparticle-surfactant complexes resulting in much smaller diffusion coefficient.

Measurements of surface pressure and standard deviations from Laplacian shape fitting during large amplitude surface area compression/expansion experiments provide very valuable information for understanding nanoparticle surfactant complexes interaction at the interface and detecting initiation of close-pack conditions. The standard deviation values detect such an initiation more accurately. The closed-pack state and the surface collapse occur at lower surface area compression with increasing nanoparticle concentration as a result of higher complex number at interface. Moreover, the rate of increases in the surface pressure before the collapse also increases with the concentration of nanoparticle and deviates from linear trend at lower surface compression.

The surfactant-nanoparticle complexes show surface activity more than similar surfactant solutions in the range of the studied cases. The complexes have a greater impact on reducing the IFT at equilibrium conditions when comparing the overall number of surfactant transferred to interface along with nanoparticles.

Acknowledgements

The authors would like to extend their sincere appreciation to Max Planck Institute of Colloids and Interfaces, German Space Agency (DLR) and Center of Applied Space Technology and Microgravity (ZARM, University of Bremen) for their general supports for the related research works and projects that have been indirectly a support for the current research work. The valuable cooperation and supports of Mr. Hamid Reza Norouzi & Mr. Hamid Heidari for this research work is appreciated.

References


Fig. 13. Dynamic foam ability of surfactant solutions (Left) and surfactant-nanoparticle dispersions (Right). The glass column diameter is the same (3 cm) in both cases but for mixture systems, pictures with a higher zoom is shown to better detection of liquid surface.