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Synergistic effect of polymer-surfactant mixtures on the stability of aqueous silica suspensions

Aylin Şakar-Deliormanlı *

Izmir Institute of Technology, Chemical Engineering Department, Urla, Izmir, Turkey

Abstract

The aim of the present work was to investigate the effect of cationic/nonionic surfactant mixtures on the dispersion and flocculation behavior of aqueous silica suspensions. In the study dodecylamine (DDA) was used as the cationic surfactant and polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO–PPO–PEO) triblock copolymers were employed as the nonionic surfactant. The dispersion and flocculation behavior of aqueous silica suspensions were studied mainly by turbidity measurements at low solids loading (0.05 vol.%) to observe the stability of the system for a given time period. Rheological measurements were performed at higher solids loadings to determine the viscosity as a function of shear rate. Adsorption behavior of single and mixed surfactants onto silica surface was studied using a total organic carbon analyzer.

Results of the study showed that dispersion and flocculation behavior of aqueous silica suspensions depends on the type and concentration of surfactant, cationic/nonionic surfactant ratio and surfactant addition sequence to the system.

Keywords: Suspensions; SiO_2; Surfactants

1. Introduction

Dispersion and flocculation of colloidal suspensions using polymers and surfactants have widespread applications and have a crucial effect in ceramic processing. The production of high-quality ceramics usually requires the preparation of stable suspensions. On the other hand, novel wet shaping methods of ceramics show the importance of investigation on the controlled flocculation of these systems. In other words, in some of the applications destabilization of the oxide particles is the main purpose; however, in other cases stabilization is desired.[1] Surfactants and polymers can dramatically change the stability of colloidal dispersions because of the interfacial activity and both an increase or decrease of the stability is possible in these systems. When polymers are used their conformation can be manipulated by changing the suspension conditions such as pH and ionic strength or addition of a second polymer or surfactant may change their activity. Such manipulation can be used to obtain desired levels of flocculation or stabilization.[2]

Several studies have been conducted to understand the adsorption mechanism from single or mixed surfactant solutions in relation to stability of metal oxide/water systems.[3,4] But there is a special interest for the investigation of ionic/nonionic surfactant mixtures. Effects related to competitive or synergistic adsorption of anionic and nonionic surfactants were observed in the flocculation studies of alumina by Esumi et al.[5] It was shown that the co-adsorption behavior at the solid liquid interface depends on the molecular structures of the co-adsorbates. For the dual systems, when the interaction between the surfactants is favorable, enhancement of adsorption of one surfactant would occur by the adsorption of another surfactant. Similarly Fan et al. have studied the co-adsorption of anionic and nonionic surfactants on and alumina.[6] It was found that the sequence of addition is crucial in determining the dispersion and flocculation behavior. Palla and Shah have been shown that the synergistic mixtures of ionic and nonionic surfactants are capable of stabilizing suspensions in which either ionic or nonionic surfactants are insufficient stabilizers.[7] As discussed by the same scientists, this kind of stabilization process is dependent on the choice of ionic and nonionic surfactant. As a consequence in literature the use of mixed surfactant solutions often results in enhanced performance and it is a synergistic process.[7,8]

Water soluble polyethylene oxide–polypropylene oxide–polyethylene oxide PEO–PPO–PEO block copolymers are characterized by good stabilization ability and have widespread

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* Tel.: +90 232 7506680; fax: +90 232 7506196.
E-mail address: aylindeliormanli@iyte.edu.tr.

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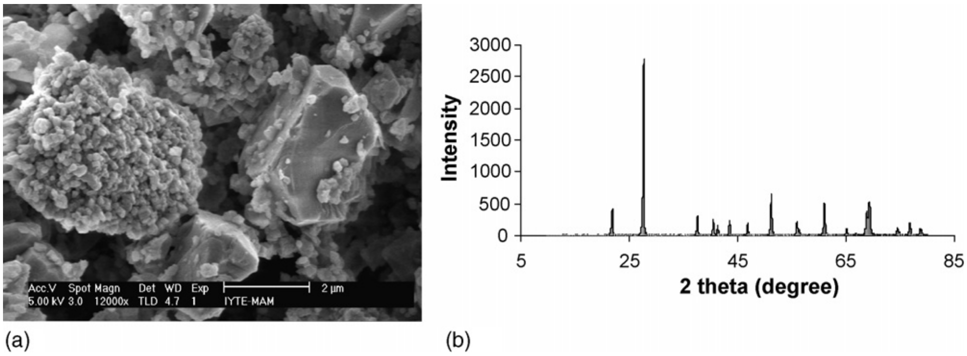

Fig. 1. (a) SEM micrograph and (b) X-ray diffraction pattern of the silica powder.

Table 1
Important properties of the block copolymers used in the study

Code	Mw	Composition	PEO (%)	Melt point (°C)	Viscosity (cps)
F127	12,600	$EO_{97}PO_{69}EO_{97}$	70	56	3100
F68	8400	$EO_{78}PO_{30}EO_{78}$	80	52	1000

applications. They consist of two hydrophilic PEO chains and a hydrophobic PPO chain and is available in different segment lengths. Although the adsorption behavior of PEO homopolymers and PEO–PPO–PEO triblock copolymers onto silica surface and rheological behavior of these systems have been investigated previously, combined effect of these polymeric surfactants with the simple cationic surfactants have not been studied in detail.[9–13] Therefore in this study it was intended to investigate the effects of PEO–PPO–PEO type block copolymer and dodecylamine DDA alone and as a mixture on the stability of aqueous silica suspensions.

2. Experimental

2.1. Materials

A commercially available silica powder, from Sigma-Aldrich Chemicals (S5631) was used in the study. The powder purity is approximately 99% and it has a wide particle size distribution. 80% of the powder is between 1–5 μm as reported by the manufacturer company. The specific surface area of the powder was measured to be 6.29 g/m^2 using ASAP 2400 Micromeritics Instrument, USA by nitrogen adsorption with multi point BET method on samples degassed at 150 °C. Isoelectric point (iep) of the silica powder was found to be at pH 2.9 using Zetasizer 3000 HSA, Malvern Instruments, UK. Fig. 1 shows the microstructure and the X-ray diffraction pattern of the silica powder obtained by scanning electron microscope, Phillips XL-30S FEG and X-ray diffraction machine Phillips X'Pert Pro, respectively.

Triblock copolymers (Pluronic F127 and F68) used in the study were obtained from BASF Corporation, Washington, NJ, USA. Some properties of these polymers are tabulated in Table 1. The cationic surfactant, dodecylamine was obtained from Aldrich Chemicals with Mw 185.4 g/mol and purity 98%. Chemical structure of the surfactants used in the study is shown in Fig. 2. Deionized water with a resistivity of 18.2 MΩ cm was used throughout the experiments. Adjustment of the pH was performed using analytical grade HCl, Merck Chemicals.

2.2. Method

In the study suspensions were prepared at different solids loadings namely 0.05, 10, and 30 vol.%. Suspension preparation and characterization methods summarized in the following paragraphs.

2.2.1. Turbidity measurements

Suspensions were prepared at 0.05 vol.% using two methods. In the first method silica powder was added into surfactant solution and stirred for 15 min using magnetic stirrer then 10 min of ultrasonic treatment and 15 min of stirring were applied subsequently. In the second method, suspensions were stirred for 24 h.

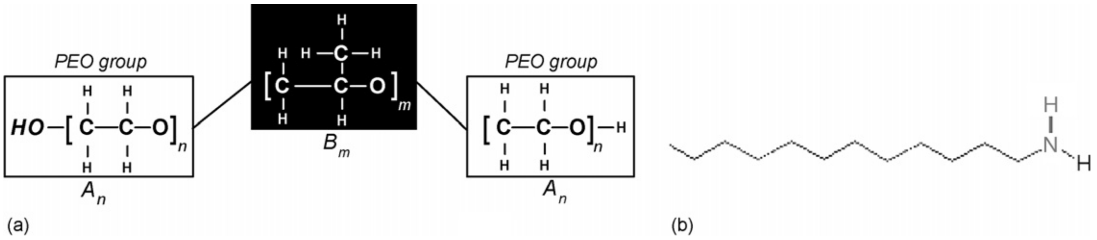

Fig. 2. Chemical structure of (a) PEO–PPO–PEO tri block copolymers (Pluronic F-127, F-68); and (b) dodecylamine.

Measurements were conducted in the range 30 s–64 min using a Turbidimeter WTW 555, Germany. Turbidity is an optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample. A turbidimeter measure the light scattered at an angle to the incident light beam and then relate this angle scattered light to the samples turbidity. Most modern instruments measure 90° scatter and they are called nephelometric turbidimeter. Turbidity measured in this way is stated in nephelometric turbidity units (NTU).[14] In the current study, turbidity measurements were performed using nephelometric ratio method and results were recorded in terms of NTU with ±2 of value or ±0.01 NTU accuracy.

2.2.2. Rheological measurements

Rheological properties of the suspensions (30 vol.%) were analyzed using a Brookfield DV-III Programmable rheometer (Brookfield, USA) with a UL adaptor and a concentric cylinder measuring unit. Suspensions were mixed for 1 week using a laboratory shaker (Gerhardt-Germany, THO 500, Incubator shaker) at a shaking frequency of 150 min^{-1} and temperature 25 °C before the measurements. Viscosities and shear stresses of the suspensions were measured at different shear rates under the following conditions:

- Initial shear rate was set at 10 s^{-1}.
- It was increased to 250 s^{-1} by 10 s^{-1} in every 30 s.
- All measurements were performed at 25(±1)°C.

2.2.3. Adsorption studies

For the adsorption studies the suspensions (10 vol.%) were homogenized and stirred for 1 week to ensure the equilibrium using a laboratory shaker (Gerhardt-Germany, THO 500, Incubator shaker) at a shaking frequency of 150 min^{-1} and temperature 25 °C. Each suspension was then centrifuged at 3000 rpm for 1 h and the supernatant solution was analyzed using a total organic carbon analyzer (Shimadzu TOC-V CPH, Japan). TOC analyses were performed in triplicate. The amounts of surfactant adsorbed obtained from the difference between the initial surfactant concentration and the equilibrium concentration measured in the supernatant. The adsorption behavior on silica was determined by comparing the data against known calibration curves.

3. Results and discussion

3.1. Stability of the system by turbidity measurements

Turbidity measurements were conducted to study the stability of silica/water system at low solids loading in the absence and presence of surfactants F127, F-68 and DDA. Fig. 3 shows the effect of pH on the stability of the silica/water and silica/water/F127 suspensions. The results showed that the pH of the medium is very effective concerning flocculation behavior. As expected particles settled around pH 2, which is very close to the isoelectric point of silica. Natural pH values of the suspensions were in the range of 6.5–7.5 and at these pH values turbidity values were high.

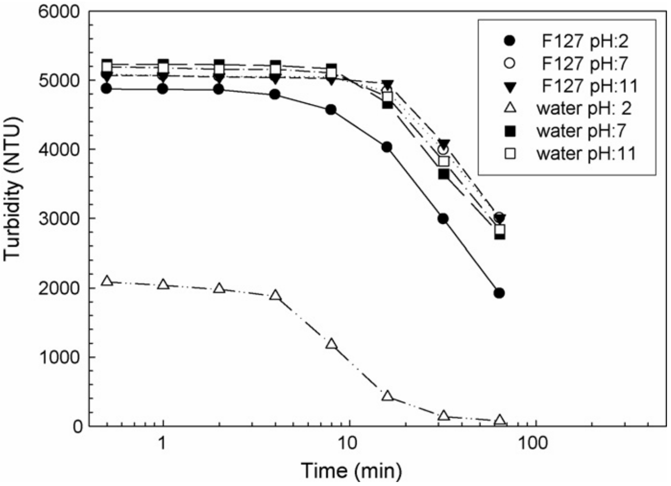

Fig. 3. Effect of pH on the stability of aqueous silica suspensions in the absence and presence of nonionic block copolymer F127 at 10^{-3} M.

Fig. 4 shows the effect of F127 and DDA alone on the stability of the aqueous silica suspensions for short mixing times (30 min). According to the results F127 provides a good dispersion; however, DDA cause flocculation at all concentrations. Similarly Wang et al. showed that the addition of DDA at 3.75×10^{-4} Mm into a fine silica suspension at pH 8 caused significant aggregation and rapid settling of silica particles.[15] This is most probably due to the adsorption of positively charged DDA onto negatively charged silica particles. Adsorption is expected to occur by electrostatic attraction and orientation of the hydrocarbon chain of the DDA molecules is towards the aqueous solution. Therefore, silica surface becomes hydrophobic and particles attract each other to flocculate.

On the other hand, turbidity values of the suspensions prepared by longer mixing time (24 h) was not the same with the turbidity values presented in Fig. 4. In this case again DDA at 10^{-3} and 10^{-4} M caused a strong flocculation the system. But also a decrease was observed in the turbidity values of the silica suspensions in the presence of F127 (Fig. 10).

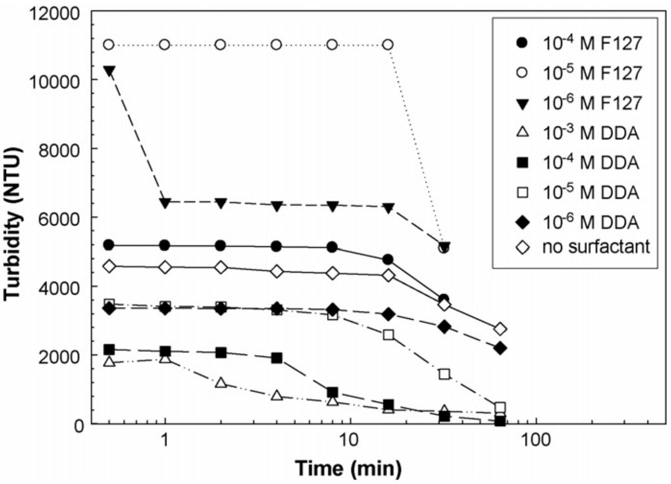

Fig. 4. Turbidity values of silica suspensions in presence of single surfactants, F127 and DDA, pH 7.

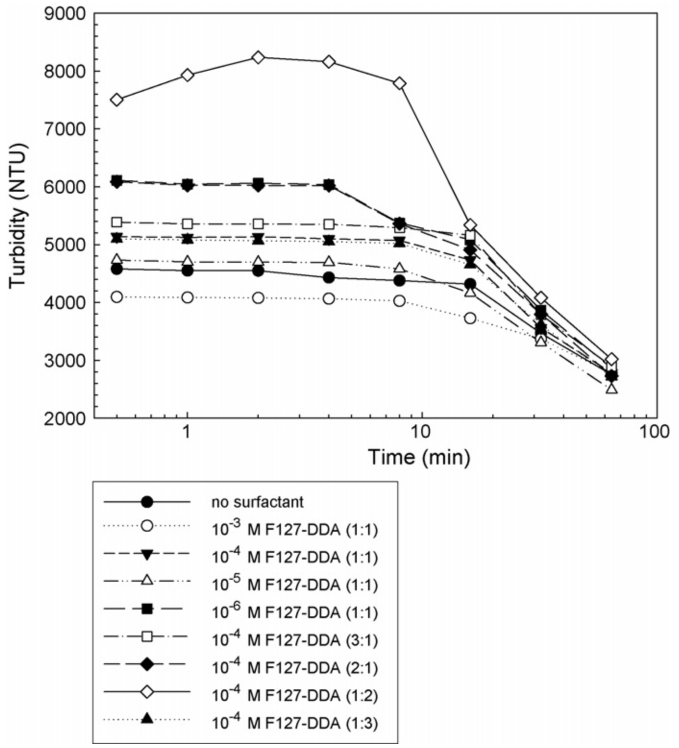

Fig. 5. Turbidity values of the silica suspensions in the presence of DDA-F127 mixture. Simultaneous addition with nonionic-ionic surfactant ratio (*x*:*y*), pH 7.

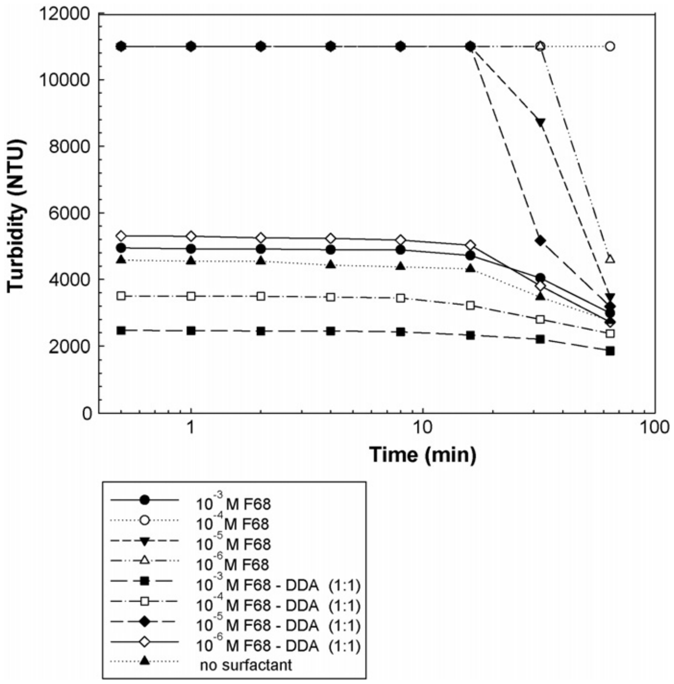

Fig. 6. Turbidity values of aqueous silica suspensions in the presence of F68 and DDA-F68 mixtures; Simultaneous addition with nonionic-ionic surfactant ratio (*x*:*y*), pH 7.

3.1.1. *Simultaneous addition*

Fig. 5 shows the effect of simultaneous addition of F127 and DDA on the stability of the system. Results indicate that simultaneous addition of F127 and DDA in an equal ratio (1:1) has a positive effect on the stability of the system for short stirring times. Only at high surfactant concentration (10^{-3} M) flocculation was observed. But as the stirring time increased since the adsorption equilibrium was reached the simultaneous addition of F127 and DDA caused flocculation almost at all concentrations.

The effect of the surfactant ratio on the stability of silica suspensions was also tested in the study. Although very high turbidity values were obtained in the case of F127 and DDA mixture at (1:2) ratio, after 16 min nearly all the surfactant mixtures having different ionic/nonionic ratios followed a similar pattern.

In the study effect of lower molecular weight nonionic F68 and cationic DAA on the stability of silica suspensions were also investigated (Fig. 6). The stability of the aqueous silica suspensions containing F68 showed similar behavior within care of F127 addition but having higher turbidity values. Turbidity values in the presence of 10^{-4} M F-68 were 11000 NTU up to 64 min. Since the F68 structure has a higher content in PEO than F127, the higher stability provided by the F68 may be attributed to this feature. Additionally, the mixture of F68 and DAA with equal ratios at 10^{-5} M again provided good stability.

3.1.2. *Preferential Addition*

In the study the effects of the addition mode of the mixed surfactants on the stability of the silica suspensions was studied using turbidity measurements. Fig. 7 illustrates the effect of sequential addition of surfactants on the stability of the system for short mixing times (30 min). According to Fig. 7 when F127 is added to the system before DDA it provides higher stability at 10^{-4} and 10^{-5} M but at high polymer concentrations, such

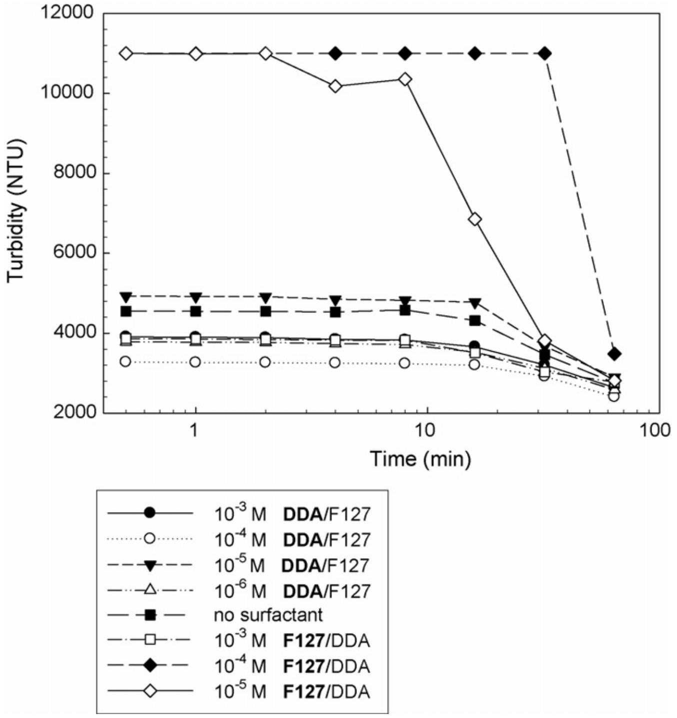

Fig. 7. Turbidity values of aqueous silica suspensions in the presence of surfactant mixtures; sequential addition with nonionic/ionic surfactant ratio (1:1), 30 min mixing, pH 7.

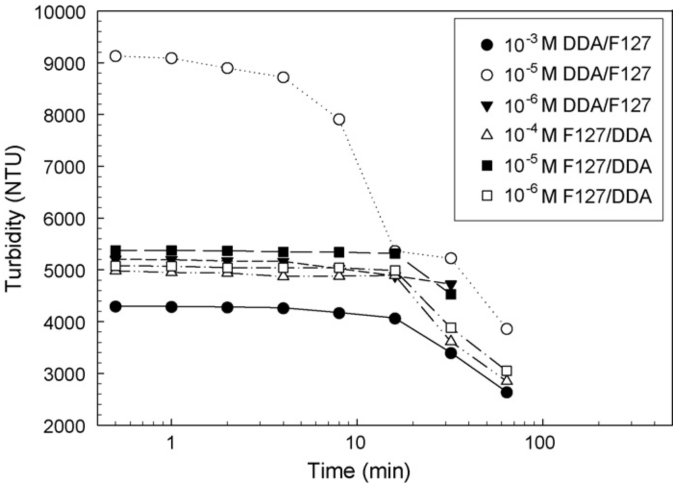

Fig. 8. Turbidity values of silica suspensions in the presence of surfactant mixtures; sequential addition with nonionic/ionic surfactant ratio (1:1), 24 h mixing, pH 7.

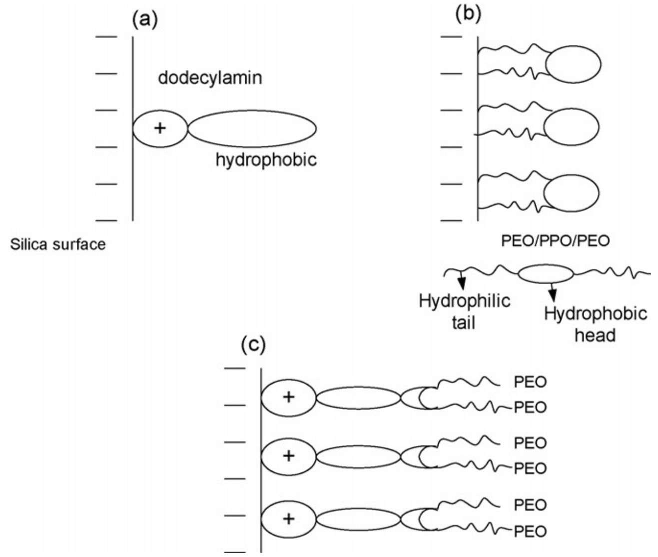

Fig. 9. Schematic illustration of the stabilization mechanism provided by the surfactant mixtures.

as 10^{-3} M it causes flocculation since this value is close to the critical micelle concentration of F127.

However, the behavior of the same system after longer mixing periods (24 hours) is not the same (Fig. 8). In this case higher stability was achieved when DDA was added to the system first followed by F127 addition. Especially at 10^{-5} M initial addition of DDA provided very high turbidity values in the silica/water system. The mechanism of the stability provided by the sequential addition of surfactants can be explained by the hydrocarbon chain interaction between cationic DDA and nonionic F127. When DDA is added to the system first it attaches to the silica surface by hydrophilic amine groups and creates highly hydrophobic surface sites on silica due to the hydrophobic dodecyl groups. On the other hand, tri-block copolymers have hydrophilic PEO groups and hydrophobic PPO groups in their structure (see Fig. 2). A possible stabilization mechanism may be the hydrocarbon chain interaction of hydrophobic PPO groups of the copolymers with hydrophobic groups of the DDA molecules. By this way hydrophilic PEO groups stay in the solution and provide larger steric barrier between the silica particles. This mechanism is shown schematically in Fig. 9.

3.1.3. *Effect of stirring time*

Results showed that the stability of the silica/water system in presence of surfactants is dependent on the stirring time of the suspensions. According to the results presented in Fig. 10 in the case of short stirring times (30 min) depletion stabilization may be dominant. It is well-known that sterically stabilized suspensions in the presence of unadsorbed polymers display depletion effects, which can induce either flocculation or stabilization. Depletion interactions are governed by the balance between the osmotic pressure exerted on the particles by the polymer solution and the size of the depletion region from which the macromolecules are expelled.[9]

In the case of long stirring times block copolymers adsorb onto the silica leading to a hydrophobic surface. This is indicated by the low turbidity values. It is also well-established that the adsorption of polymers on most surfaces is irreversible resulting in the so called high affinity adsorption.[16] Therefore, the decrease of the turbidity values after longer stirring time cannot be explained by the desorption mechanism. Fig. 10 shows the effect of mixing time on the stability of silica suspensions in the presence of F127.

Results of the current study also agree well with the findings of a previous study which was carried by Whitby et al.[17] According to the results of this previous study adsorbed PEO layers impart steric stabilization to silica dispersions. Some evidence was also found for depletion interactions in the presence of significant concentrations of unadsorbed PEO. At low PEO coverage of silica, attractive bridging forces were measured between silica surfaces while at higher coverage, repulsive steric interactions were observed.[17]

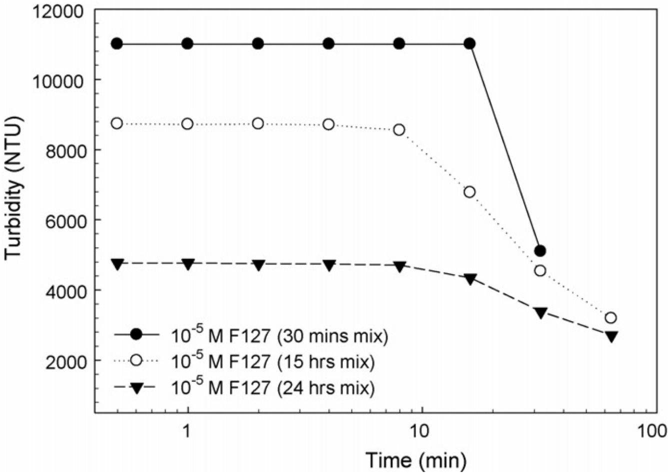

Fig. 10. Effect of stirring time on the stability of aqueous silica suspensions in the presence of F127 at pH 7.

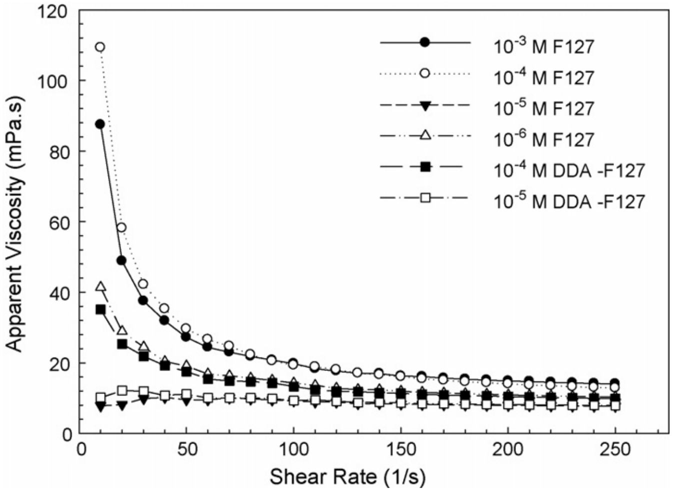

Fig. 11. Viscosity vs. shear rate graph for aqueous silica suspensions in the presence of F127 and DDA-F127 mixture. Simultaneous addition with nonionic-ionic surfactant ratio (1:1), pH 7, solids loading 30 vol.%.

3.2. Rheological measurements

The stability of the silica suspensions could be related to the rheological properties of this suspensions. In the current study rheological behavior of the aqueous silica suspensions in the absence and presence of surfactants were studied at 30 vol.% solids loading and pH 7. Typical examples of the flow curves are given in Figs. 11 and 12. It is interesting to observe that simultaneous addition of DDA-F127 mixture at (1:1) ratio to the silica/water system provided lower viscosities at 10^{-4} and 10^{-5} M compared to the values of the suspensions in the presence of single surfactants. The flow characteristics of the suspensions containing 10^{-3} and 10^{-4} M, nonionic F127 fits with the Bingham flow model with a yield stress 0.93 and 0.55 N/m^2, respectively. The similar behavior was observed also for the suspensions containing DDA-F68 mixture at (1:1) ratio. At certain concentrations (10^{-5}, 10^{-4} M) simultaneous addition of F68 and DAA mixture to the silica/water system provided very low viscosity values.

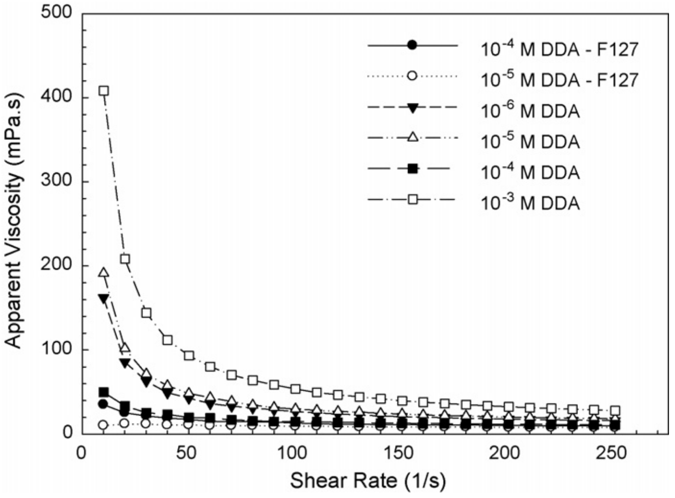

Fig. 12. Viscosity vs. shear rate graph for aqueous silica suspensions in the presence of DDA and DDA-F127 mixture. Simultaneous addition with nonionic-ionic surfactant ratio (1:1), pH 7, solids loading 30 vol.%.

On the other hand, according to Fig. 12, the flow curve of the aqueous silica suspension containing DDA at 10^{-3} M fits with the Casson Model (yield stress 2.77 N/m^2). At lower DDA concentrations such as 10^{-5} and 10^{-6} M Bingham flow model was consistent. Yield stresses observed in the Figs. 11 and 12 may be attributed to the wider particle size distribution or the rough non-spherical morphology of the quartz particles. Flow characteristics of the suspensions can be explained by the formation of flocs in the structure. When the attractive forces between particles prevail, collisions among them will lead to the formation of agglomerates. At low shear rates, liquid is immobilized in void spaces within flocs and floc network. As the shear rate is increased, the flocs break down the entrapped liquid is released and a more ordered structure in the flow direction is formed.[18]

3.3. Adsorption studies

The results of the adsorption studies of single and mixed surfactants DDA, F127 and F68 onto silica surface is presented in Fig. 13. Results showed that adsorption of PEO–PPO–PEO onto silica surface depends on the molecular weight and the PEO/PPO ratio (Fig. 13). Higher molecular weight of a copolymer means higher flexibility of the entire molecule. This increase flexibility offers a better protection of the PPO block (toward to the aqueous environment). But if we compare the adsorption behavior of F127 and F68 as it is seen in Fig. 13, F68 with lower molecular weight and higher PEO portion (PEO/PPO: 80/20) showed higher adsorption onto silica surface than the F127.

Hydrogen bonding between the ether oxygen and the silanol groups of the silica surface is responsible for the adsorption of the block copolymers onto the silica surface. In a previous study Kawaguchi et al.[10] explained the adsorption of the same type of block copolymers by the hydrogen bonding between the ether oxygen and the silanol groups of the silica surface leading to suppression of an aggregated structure of the silica particles, in water maintained through interaction between silanol groups on the silica surface. Calorimetric data for the adsorption of nonionic surfactant nonyl phenol ethoxylate on silica suggest adsorption with part of their oxyethylene head on the solid and the other part in the bulk. Spectroscopic evidence exits for hydrogen bonding between polyethylene oxide groups from nonionic surfactants and the hydroxyl groups at the silica surface.[19]

In the current study, adsorption of positively charged DDA onto negatively charged silica was studied in the same way with the block copolymers. Especially at high concentrations such as 10^{-3} M, DDA created highly hydrophobic surfaces. Wang et al., showed the enhance transfer of DDA molecules onto the silica surface by surface tension measurements.[8] A similar surface tension was observed with and without centrifuging the silica suspensions, confirming a negligible transfer of the adsorbed surfactant from the solid surface. However, in the current study results showed that adsorption of 10^{-3} M DDA onto silica surface was not negligible.

According to Fig. 13, highest adsorption percentage was obtained in the case of simultaneous addition of DAA-F127 or

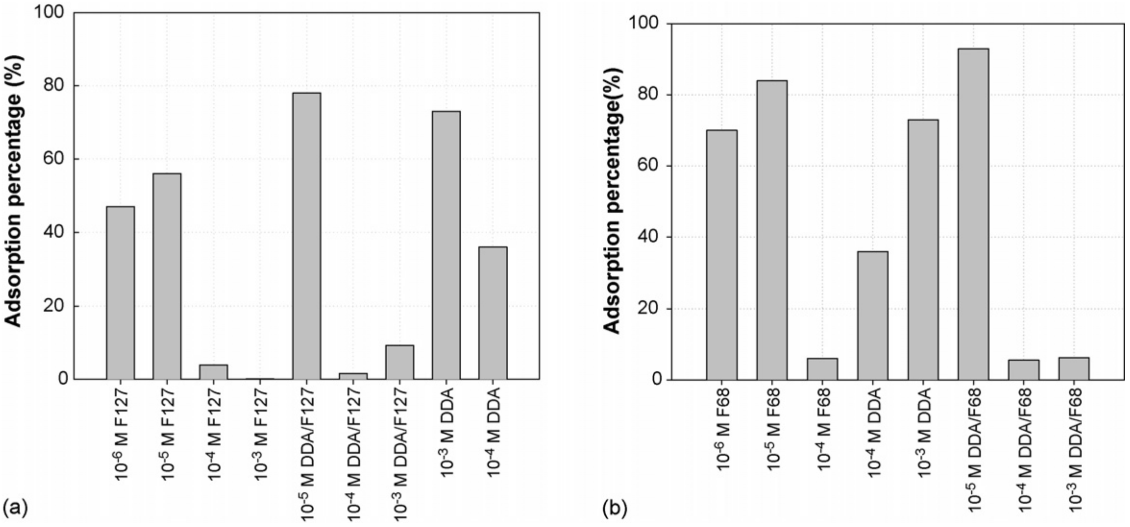

Fig. 13. Adsorption percentage of ionic and nonionic surfactants and surfactant mixtures (a) DDA-F127 (b) DDA-F68 onto silica surface, pH 7, solids loading 10 vol.%, temperature 25 °C.

DAA-F68 mixture at 10^{-5} M and (1:1) ratio to the silica/water system. In the same way stability of these systems was high as discussed in the previous sections. The possible stabilization mechanism provided by the ionic/nonionic surfactant mixtures used in this study is shown in Fig. 9. According to this mechanism first DDA adsorb onto silica surface with full surface coverage via the electrostatic attractions and make silica surface hydrophobic due to dodecyl group. It is followed by the nonionic surfactant adsorption due to PPO group onto DDA molecules via hydrophobic effect. The stabilization is brought by the steric barrier created by the hydrophilic PEO group of the nonionic surfactant extending into the solution.[7,20]

4. Conclusions

- The effect of dodecylamine/block copolymer mixtures on the dispersion/flocculation behavior of aqueous silica suspensions was studied. Turbidity values of the silica suspensions in the presence of single block copolymers showed a time dependent behavior. Very high turbidity values of silica suspensions containing block copolymers in the first time interval was attributed to the depletion stabilization mechanism. As the time proceeds silica surface became hydrophobic and the turbidity values lowered. Similar effect was observed in the case of suspensions containing cationic surfactant/block copolymer mixture at different ratios.
- The cationic surfactant/block copolymer addition sequence strongly affected the stability of the system. Higher turbidity values were obtained when DDA was added to the system first followed by F127 or F68 addition.
- Adsorption studies showed that adsorption of surfactants onto silica surface has a maximum at 10^{-5} M for F-127 and F68 and at 10^{-3} M for DDA, respectively. The adsorption amount increases in the case of suspensions containing DAA-F127 and DAA-F68 mixtures.
- A possible stabilization mechanism of ionic/nonionic mixtures in silica/water system is the adsorption of block copolymers to cationic surfactant due to strong hydrophobic interactions, which also enhance the stability of the system and have synergistic effects.

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