Effect of Surfactant and Polymer Adsorption on the Viscosity of Aqueous Colloidal Silica Dispersions under Extreme Conditions

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Abstract

The effect of surfactant and polymeric additives on the viscosity behavior and stability of aqueous colloidal dispersions of silica particles under extreme conditions (low pH, high ionic strength) has been investigated. The surfactant and polymer used as dispersing agent were C₁₂TAB, a cationic surfactant, and DarvanC, a commercially available polymer. It was found that the surfactant stabilized dispersions show a lower viscosity and a more uniform resistance to flow than the samples stabilized through electrostatic repulsion or polymer induced forces in the system. Stability analysis through turbidity measurements indicated that the state of the dispersion changes from an unstable regime to a stable regime above a critical concentration of C₁₂TAB in the system. Viscosity measurements as a function of temperature indicates that C₁₂TAB dispersing agent can further improve the flowability of the dispersion at higher temperatures.

1. Introduction and Background

Stability and viscosity behavior of concentrated colloidal dispersions of solids is determined by the combined effects of different factors such as Brownian motion of the particles, hydrodynamic interactions, interparticle forces, as well as physical characteristics of the particles such as particle size, particle size distribution, and shape of the particles. Colloidal dispersions are encountered in various industrial processes such as paints, paper coatings, ceramic and minerals, chemical-mechanical polishing, and pharmaceuticals. In most of the applications, colloidal dispersions need to be stabilized against aggregation and agglomeration of the particles using stabilizing agents such as salt, surfactants, polymers, and polyelectrolytes. Particle-particle interactions arising from the adsorbed and dissolved polymers and surfactants as well as van der Waals attractive forces and electrostatic repulsive forces due to the diffuse part of the electrical double layers around the charged particles play a very significant role in governing stability and rheological behavior of colloidal dispersions.

Even though the topic of electrostatic stabilization has been extensively studied by many investigators (1-3) and the DLVO theory is now largely accepted as a classical description for stability of colloidal dispersions through electrostatic repulsion, but when surfactants and polymers are used as stabilizers, surfactant interactions and steric forces do not fit this theory leaving a problem of both experimental and theoretical interest.

Additionally, the increasing use of suspensions of nanosized particles in severe environments such as high electrolyte concentrations, high pressures, high shear and high pH levels in applications such as chemical mechanical polishing, consolidation, pumping, deaggregation, grinding, homogenization, high speed coatings, and crystal growth necessitates the development of versatile dispersants capable of dispersing the nanoparticles under severe environments. At high salt concentrations, electrostatic repulsive forces will be of very short range and do not protect the colloidal particles against coagulation. Stabilization of such dispersions may be achieved through the addition of surfactants as dispersing agents to the suspending media. It is very important to identify the conditions (dosage, pH, etc.) at which the added surfactant will stabilize the system.

Electrostatic repulsion is often applied to stabilize dispersions of solid particles at low levels of ionic strength where pH can be controlled in order to pro-
Sufficient surface charge. Considering that the electrostatic repulsive energy between the suspended particles decreases as the size of the particles is decreased, a greater surface potential is required to stabilize dispersions of nanoparticles of smaller sizes. Under these conditions, pH adjustment or addition of inorganic dispersants such as sodium silicate may not lead to a dispersion of sufficient stability against aggregation and agglomeration of the particles.

Since most of the traditionally used polymeric dispersants are similar in size to the nanoparticles, hence in the case of highly concentrated dispersions, there will be a significant increase in the effective volume fraction of the particles that may adversely affect the fluidity of the system. When polyelectrolytes are used as stabilizing agents, stability will be imparted through a combination of electrostatic and steric repulsion. At high electrolyte concentration and extreme pH conditions, these dispersants may not perform adequately due to charge neutralization and insufficient ionization.

Surfactants provide a viable alternative for stabilization of the dispersions of nanoparticles under extreme conditions due to the small thickness of the adsorbed surfactant layer, controlled adsorption, and reversibility of adsorption. Surfactants have been used in various industrial processes ranging from ore flotation, lubrication, and paint technology to enhanced oil recovery (4). Forces between surfactant coated surfaces have been measured by several investigators (5-7) in order to understand the surfactant adsorption and also to predict the nature of the aggregate formed by surfactant molecules on surfaces. Also, surfactants have been used for the dispersion of particulates in aqueous media by researchers such as Evanko et al (8), Huang and Somasundaran (9), Colic and Fuerstenau (10), Colic and Fuerstenau (11), Koopal et al (12), Bremell et al. (13), and Solomon et al. (14). In this work a systematic study has been performed on the role of surfactants (as dispersing agents) on stability and fluidity of colloidal aqueous silica dispersions at high electrolyte concentrations.

2. Methods

Silica powder of 99.9% purity used in this study was obtained from Geltech, Inc. The powder was used as received and had a nominal diameter of 200 nm, as stated by the manufacturer. The experimentally measured volume average (d50) particle diameter (using a Coulter LS230 laser diffraction apparatus) of the powder was found to be 250 nm. Powder density and surface area were found to be 2.1 g/cm³ and 14.62 m²/g respectively.

Dodecyltrimethylammonium bromide (C₁₂TAB) of 99% purity was obtained from Aldrich Chemical Company and used as received. Surfactant stock solutions of different concentrations were prepared in an electrolyte solution of 0.1 M Fisher brand NaCl and stirred using a magnetic stirrer in order to achieve complete dissolution. The surfactant dosage was calculated so that the bulk concentration of the surfactant, i.e. surfactant left in the suspending fluid after adsorption onto the surface of the particles was 32 mM at all solids loading. For suspensions of 250 nm silica particles at 45 %vol and 50 %vol the surfactant concentration was determined to be 250 mM and 300 mM respectively. The CMC (critical micelle concentration) of Dodecyltrimethylammonium bromide (C₁₂TAB) was determined to be 8 mM with 0.1 M NaCl and at a value of CMC, the surfactant aggregate structure is very stable and can provide steric barrier to the agglomeration of the particles. All experiments were conducted in ultra pure water (DI) of specific conductivity less than 1 μohm/cm. Sodium chloride (NaCl) was used as background electrolyte and sodium hydroxide (NaOH) and Hydrochloric acid (HCl) were used as pH modifiers. These reagents were of ACS grade and obtained from Fisher Scientific Company.

Silica slurries were prepared by gradually adding silica powder to the electrolyte or electrolyte-surfactant solutions. The required mass of dry silica (to prepare 10 cm³ of the suspension at a given volume fraction of the particles) was then slowly added to the solution while mixing the sample by shaking and vibration. After addition of silica, the suspensions were vigorously shaken by hand and then the pH of the samples was adjusted to 4 using HCl solution. After the pH adjustments, samples were sonicated for at least 30 minutes in order to break up any aggregates. The suspensions were then agitated using a Burrell Model 75 Wrist Shaker for a period of 16–20 hours in order for equilibrium to be reached. During equilibration, the pH of the suspensions was checked periodically and readjusted if required.

Viscosity measurements were carried out using a Paar Physica UDS 200 rheometer with a cone-and-plate geometry. All experiments were performed at 25°C and the sample temperature was controlled to within ±0.1°C using water as the heat transfer fluid. In all experiments, a cone of radius 4.30 cm with a cone angle of 0.5° (a gap size of 25 μm) was used. Viscosity measurements as a function of time (at a fixed shear rate) indicated that sedimentation of the particles and
Water evaporation from the samples during experiments were negligible. To check for other possible errors (e.g., inertial and secondary flows, edge effects, etc.), some of the experiments were repeated using a cone of radius 3.75 cm with a cone angle of 1.0° (a gap size of 50 μm). The results did not change over the time period of experiments and the viscosity values measured with two different cones agreed within experimental error (±3%).

Stability analysis on the samples was performed by measuring turbidity of the dispersions as a function of time and surfactant concentration using a Hach Model 2100AN turbidimeter. The optical system of the instrument consists of a tungsten filament lamp, lenses, and apertures to focus the light, a 90° detector to monitor scattered light, a forward-scatter light detector, a transmitted light detector, and a back scattered light detector.

For turbidity measurements, samples were prepared by adding 0.05 grams of silica particles to 50 ml of suspending fluid (surfactant solutions of different concentrations in 0.1 M NaCl solution). Samples were then sonicated for 10 minutes and the pH of the dispersion was then adjusted to 4.0 using Fisher brand HCl. The suspensions were then allowed to shake for 2 hours on a wrist shaker and if needed the pH was re-adjusted to 4.0 prior to the turbidity measurements.

Zeta potential measurements were carried out using a Laser Zee Meter (Model 501) instrument supplied by PenKem Inc. Using this instrument, zeta potential is determined based on electrophoresis phenomena. In this method, the velocity of multiple particles with respect to a stationary fluid is measured in a potential gradient applied between platinum and molybdenum electrodes using a rotating prism and then used to determine the zeta potential.

For zeta potential measurements, silica slurries were prepared by adding 0.1 grams of 250 nm (diameter) silica particles to 50 ml of suspending media following the same procedure that was explained in preparing samples for turbidity measurements.

3. Results
3.1 Zeta Potential

Figure 1 presents zeta potential as a function of surfactant concentration for suspensions of 250 nm (diameter) silica particles dispersed in a 0.1 M NaCl solution (suspension pH=4). When a cationic surfactant such as C_{12}TAB is added to the dispersion of charged particles, electrical double layer around the particles and therefore, the zeta potential will be altered due to the adsorption of surfactant molecules onto the surface of the particles. It can be observed from Figure 1 that while at low levels of C_{12}TAB concentration (less than 2.5 mM) the zeta potential values indicate a negative charge on the surface of the particles, at higher levels of surfactant concentration, silica particles will be positively charged and there will be an increase in the magnitude of the zeta potential as particles are gradually covered by surfactant molecules.

The zeta potential of the bare silica surface at pH 4.0 in the presence of 0.1 M NaCl is approximately equal to −10 mV. It can be observed that, as the amount of surfactant added to the dispersion is increased, there is no observable change in the zeta potential till a critical concentration of C_{12}TAB, which appears from the data given in Figure 1 to be approximately equal to 0.6 mM. Beyond this concentration which is equal to critical hemi-micelle concentration (15), the original charge of the surface is neutralized by the adsorption of oppositely charged surfactant by ion pairing. The surface charge eventually acquires the same sign as the surfactant ion (positive in the case of C_{12}TAB) due to formation of bilayers of the surfactant molecules. As the surfactant concentration is increased further (beyond 8 mM surfactant concentration), the rate of adsorption decreases due to repulsion between oncoming ions and similarly charged particle surface and finally saturation adsorption is achieved. Correspondingly, the slope of the zeta potential curve also decreases and finally the zeta potential reaches a plateau value of +45 mV.

3.2 Stability of Dilute ΣiO_{2} Dispersions in the Presence of C_{12}TAB

Based on the DLVO theory of colloidal stability, an important factor influencing stability of aqueous
colloidal dispersions is the surface potential of the particles. The repulsive interactions between the suspended particles hinder aggregation and agglomeration of the particles providing a certain degree of stability. Effect of C_{12}TAB concentration on the stability of dilute SiO\textsubscript{2} dispersions prepared in an electrolyte solution of 0.1 M NaCl (suspension pH=4) was evaluated through measurement of the turbidity of the dispersion as a function of time. Turbidity of the dispersion in the absence of C_{12}TAB was very low indicating a high sedimentation rate of solids due to the presence of aggregates in the system. Above a critical concentration of C_{12}TAB in the system, there was a significant increase in the turbidity of the dispersion indicating a transition from an unstable regime to a stable regime after which the turbidity attained a constant value indicating no significant change in the stability of the system.

### 3.3 Shear Flow Properties

Stability and rheological behavior of colloidal dispersions can be significantly affected by the adsorption of surfactant molecules onto the surface of the particles (16). Dispersions of colloidal particle can show different rheological behavior such as shear thinning, shear thickening, yield stress, and viscoelasticity depending upon the general characteristics of the system. (17-19). **Figure 2** is a plot of viscosity as a function of shear rate for suspensions of 250 nm silica particles at solids loading of 45 %vol and 50 %vol prepared in aqueous solutions of 0.1 M NaCl containing 250 mM and 300 mM C_{12}TAB respectively (suspension pH=4). The viscosity shows changes with both shear rate and volume fraction of the particles. Both samples exhibit non-Newtonian behavior and there is no indication of shear thickening behavior over the entire range of shear rate investigated (1 s\textsuperscript{-1} up to 15,000 s\textsuperscript{-1}). While we were not able to prepare a dispersion of 50 %vol silica particles in an electrolyte solution of 0.1 M NaCl in the absence of C_{12}TAB, addition of surfactant to the suspending media made it possible to prepare a well dispersed slurry of low viscosity.

**Figure 3** is a comparison between the viscosity of dispersions of 250 nm silica particles at 45 %vol prepared at two different conditions. The first sample was prepared in an electrolyte solution of 0.001 M NaCl without the addition of surfactant and the second sample was prepared in an electrolyte solution of 0.1 M NaCl and 250 mM C_{12}TAB (the pH of both samples was adjusted to 4). While the first sample is stabilized through long range electrostatic repulsion between the suspended particles, the second sample is stabilized through surfactant induced forces due to the adsorption of C_{12}TAB molecules onto the surface of the particles. There is a significant difference between the viscosity of the two samples even at very high shear rates where hydrodynamic forces are dominant. Surfactant stabilized dispersion shows a lower and a more uniform resistance against flow than electrostatically stabilized dispersion. This indicates that C_{12}TAB is a more effective dispersing agent for silica slurries under extreme condition.

The data presented in **Figure 3** indicate that the differences between the viscosity of the samples are more significant at low shear rates. Suspensions of particles in shear flows experience different kind of forces such as hydrodynamic forces (including the viscous drag force and particle-particle interaction through flow field induced by neighboring particles), colloid chemical forces (including electrostatic, steric, and London-van der Waals attractive forces), forces

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**Fig. 2** Viscosity as a function of shear rate for 250 nm (diameter) dispersions of silica particles of 45 %vol and 50 %vol stabilized with C_{12}TAB (0.1 M NaCl, 25°C and suspension pH=4).

**Fig. 3** Comparison between the viscosity of electrostatically stabilized (0.001 M NaCl) and surfactant stabilized (0.1 M NaCl, 250 mM C_{12}TAB) dispersions of 250 nm (diameter) silica particles of 45 %vol (25°C and suspension pH=4).
3.4 Effect of Temperature on the Viscosity and Stability of SiO$_2$ Dispersions in the Presence of C$_{12}$TAB

Figure 4 represents the effect of temperature on the viscosity of a 50 %vol dispersion of 250 nm silica particles prepared in an electrolyte solution of 0.1 M NaCl containing 280 mM of C$_{12}$TAB surfactant (suspension pH=4) at a shear rate of 50 s$^{-1}$. It can be seen that over the temperature range studied, the viscosity of the dispersion initially decreases with increasing temperature, reaches a minimum at approximately 55°C and then increases with further increase in temperature. This indicates that C$_{12}$TAB dispersing agent can further improve the flowability of the dispersion at higher temperatures. Increase in temperature will increase Brownian motion of the particles which is in favor of increasing the viscosity of the dispersion due to increase in number of collision between the suspended particles. On the other hand there will be a decrease in the viscosity of the suspending fluid with increasing temperature, which tends to decrease the viscosity of the dispersion over the entire range of temperature. When surfactants are present in the system, change in temperature will affect several other important factors such as intermolecular interactions between solvent and solutes (e.g., hydrogen bonding), cmc of surfactant, and micellization. It is shown by Flockhart (20) that the cmc of most ionic surfactants goes through a minimum as the temperature is increased from 0°C to 70°C. Also, it was found by Cook et al. (21) that cmc of some nonionic surfactants is minimum around 50°C. These indicate that one needs to have a clear understanding of the effect of temperature on all the above mentioned factors to be able to explain the effect of temperature on the viscosity of the dispersion. However, this needs to be further investigated.

3.5 Effect of the Type of the Stabilization on the Viscosity of Silica Dispersions

Another method that is widely used to improve the rheological properties and stability of colloidal suspensions is the addition of polymers to the system. When water soluble polymers are added to the suspension, the polymer may be adsorbed on the particle surface. The distribution of the polymer molecules in the solution is affected by particle-particle interactions producing a force whose sign and magnitude depends on the nature of the particle-polymer interaction (22). The adsorbed polymer can either stabilize or destabilize the suspension depending upon the magnitude of the repulsive forces between the adsorbed polymer molecules. Steric stabilization occurs when the repulsive forces overcome the attractive van der Waals forces acting between the particle surfaces.

The effect of DarvanC, a commercially available polymeric dispersant on the viscosity of silica suspensions is presented in Figure 5 which is a plot of viscosity as a function of polymer dosage for aqueous silica slurries at 50 %vol (dispersed in a solution of 0.1 M NaCl and suspension pH=4) at different shear rates. It can be observed that the viscosity of the suspension initially decreases to a minimum with increasing the polymer dosage and then starts to increase with
further addition of polymer to the suspension. There is a critical amount of polymer (5 mg/g solids for the system under consideration) that must be added to the system to achieve minimal viscosities. It can be seen from this figure that the effect of polymer dosage on the viscosity of the system is more significant at lower shear rates as might be expected.

Figure 6 is a comparison between the viscosity of the above mentioned system with the viscosity of a dispersion of silica particles in the presence of C12TAB as stabilizing agent. Even though at very high shear rates the viscosity of the two systems tends to approach a final limiting value, but surfactant stabilized dispersion shows a lower resistance to flow at low to intermediate shear rates as the viscosity of surfactant stabilized system is significantly lower than the viscosity of the dispersion in the presence of DarvanC. This indicates that C12TAB surfactant is more effective than the polymeric dispersant in terms of improving the low to intermediate shear flow properties of the dispersion.

Summary

The role of surfactant and polymer adsorption on flow properties and stability of concentrated aqueous silica dispersions under extreme conditions has been investigated. DarvanC, a commercially available polymer and C12TAB, a cationic surfactant were used to stabilize dispersions of silica particles under high ionic strength and low pH. It is shown that surfactant stabilized silica dispersions show a better fluidity and a more uniform resistance to flow than the samples stabilized through electrostatic repulsion or polymer induced forces in the system.

As the amount of surfactant added to the dispersion is increased, while there is no significant change in the magnitude of the zeta potential below a critical concentration of the surfactant (critical hemi-micelle concentration), the negative zeta potential of the particles will go through zero as the surfactant concentration is increased and finally will approach a final limiting value at higher surfactant concentrations. Stability analysis through turbidity measurements indicated that while sedimentation rate of the solids is very high at low levels of surfactant dosage (low turbidity), as the surfactant concentration is increased, there will be a significant increase in turbidity of the samples indicating that the state of the dispersion changes from an unstable regime to a stable regime above a critical surfactant dosage. Zeta potential measurements as well as turbidity measurements indicate that both zeta potential and turbidity will attain constant values at high surfactant concentrations.

Effect of temperature on the viscosity of 50 %vol silica dispersion prepared in the presence of surfactant was also studied. Over the temperature range studied, the viscosity of the dispersion initially decreased with increasing temperature, reached a minimum at approximately 55°C and then increased with further increase in temperature. Since change in temperature will affect several important parameters such as Browninan motion of the particles, viscosity of the suspending fluid, intermolecular interactions between solvent and solutes, cmc of surfactant, and micellization, the combined effect of temperature on all these variables should be considered to be able to explain the effect on the viscosity of the dispersion.

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