Stability of Silica Nanoparticle Dispersion in Brine Solution: an Experimental Study

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Abstract
Nanotechnology has various applications in oil and gas industry such as enhanced oil recovery (EOR). The main challenge in using nanoparticles in EOR processes is their stability in harsh conditions such as high temperature, high pressure, and intermediate to high salinity. However, most of the recent experimental works have been performed under unrealistic conditions such as the use of distilled water as the injected fluid and room temperature. The main objective of this work is to study the effect of these factors on the stability of nanoparticle dispersions through several methods such as direct observation, optical absorption measurement, and nanoparticle effective diameter in different periods of time. The critical salt concentration (CSC) was determined for two kinds of monovalent electrolytes in various particle concentrations and temperatures. The results have shown that CSC for potassium chloride (KCl) is less than sodium chloride (NaCl) and it decreases as nanoparticle concentration and temperature increase. Moreover, the influence of two types of surfactants on the stability of silica dispersions was studied and the results revealed that an anionic surfactant increases the CSC, while a nonionic surfactant leads to the instability of dispersion even at low electrolyte concentrations.

Keywords: Silica nanoparticle, Dispersion stability, Temperature, Salinity, Surfactant

1. Introduction
Due to the rapid increase of worldwide oil demand, conventional exploration and production techniques might not be sufficient to attend to this demand (Cocuzza et al., 2011). Hence, the current major challenge is how to get the most out of the current available resources through EOR processes. Nanotechnology can introduce useful solutions to these challenges. The U.S. National Nanotechnology Initiative (NNI 2000) and other sources describe nanotechnology as a technology for synthesizing nanomaterial by controlling single atom behavior at the molecular level and creating new molecular structures. Nanotechnology refers to a field of applied science and technology in which the critical length scale is generally 100 nanometers or smaller (Krishnamoorti 2006). Although the bulk materials have constant physical properties, the properties of materials change as their size approaches the nanoscale.

Recent experimental works have shown that nanotechnology may increase the average global recovery factor of oil and gas by 10% in the near future (Tippee 2009). The major challenge in using nanoparticles in oil fields is their exposure to harsh reservoir conditions such as high salinity of
injected water, high temperature, and high pressure. It is difficult to control the stability of nanoparticle dispersion in such conditions.

The stability of aqueous nanoparticle dispersion happens when the number of particles in a unit volume is independent of time (Kissa 1999). The stability of nanoparticles in porous media is affected by several factors like pressure, temperature, the particle size, and ions or molecules present in the system. Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (Derjaguin and Landau 1941; Verwey and Overbeek 1948) can predict the stability of colloidal particles by modeling the competition between electrostatic repulsion and van der Waals attraction among such particles (Ke and Stroeve 2005; Hamedi Shokrlu and Babadagli 2011; Khilar et al., 1998; Ayatollahi and Zerafat 2012). The main purpose of the classical form of this theory is to discuss the effect of electrolyte valence and concentration on stability. The aggregation occurs whenever the Brownian motion and the attractive forces of the particles are greater than the repulsive forces. Conversely, the particles will remain separate and maintain a dispersed state when the repulsive forces are greater than the attractive ones.

The thickness of the diffuse electrical layer is one of the main factors to determine the stability of nanoparticle dispersions against aggregation. A thick diffuse electrical layer and consequently great electrostatic repulsion between particles leads to more stable dispersion. The thickness of the diffuse electrical layer is closely related to the concentration of the electrolyte present in the solution. If the concentration of the electrolyte increases, the thickness of this layer decreases and particles tend to aggregate. Thus, it is not strange to expect an increase in the aggregation of nanoparticles in saline environments like in many oil reservoirs. In addition, electrostatic forces strongly depend on ionic strength. In nanoparticle suspensions, particles tendency to aggregate more quickly at higher ionic strengths is obvious (Kallay and Žalac 2002; Kobayashi et al., 2005). The size of the electrical double layer of particles reduces as ionic strengths increase. This decreases the repulsive forces between particles. With regard to the fact that repulsive forces prevent the aggregation of particles, large ionic strengths therefore allow the attractive Vander Waals forces to dominate, and dispersion tends to become unstable and sediment (Saleh et al., 2008).

Temperature plays a kinetic role in nanoparticle dispersion stability. An increase in the average kinetic energy with temperature gives rise to the particle collisions which result in aggregation (Paul McElfresh et al., 2012).

Covering and treating the inorganic particles (e.g. silica) with organic molecules to decrease the aggregation trend can be considered as a good solution (Ke and Stroeve 2005). Surfactants, by reducing the interfacial activity, retain the particles in aqueous phase and consequently improve the dispersion stability. Stable nanoparticle suspensions were also attained by the addition of low amounts of polymers (Luis Villamizar et al., 2010).

The structure of the silica surfaces and associated water molecules, which define the characteristics of the near surface region, affect the stability of silica dispersions (Zhuravlev 1987; Yalamanchili et al., 1996; Asay and Kim 2005). The presence of silanol groups (Si-OH) on a silica surface was proposed by Hofmann in 1934. These hydrophilic silanol groups on a silica surface act as binding sites (H+ bonds) for water.

By the experimental observations of silica gels, aerogels, and porous glasses, Zhuravlev (1987) indicated that the surface of silica was fully hydroxylated, and that the OH groups corresponded to one surface Si atom were mostly comprised of a silanol group. The protonation and deprotonation of these silanol groups determine the surface charge of silica nanoparticles and the extent of the repulsive energy to keep them dispersed in the solution. For a given surface charge, the aggregation of
silica nanoparticles occurs because of the presence of electrolytes. The increasing rate of aggregation of silica nanoparticles with the concentration of electrolytes is known but not well understood (Roberts 2006). The interparticle interactions of two silica nanoparticles have recently been investigated through molecular simulations to understand the stability of dispersion (Jenkins et al., 2007, 2008; Lane et al., 2009). One of the main factors affecting the ordering of water molecules around the silica surface and the particle-water interactions is the electrical surface charge of silica nanoparticle in the presence of background sodium concentration (Na’), which has been concluded by Jenkins et al. (2007, 2008) (oscillatory interparticle forces). Lane et al. (2009) studied the forces acting on surface coated silica nanoparticles and concluded that surface coating suppressed the force oscillations. Metin et al. (2010) have shown that the CSC depends on electrolyte type, but is not influenced by silica nanoparticle concentration; Moreover, they concluded that an increase in temperature from 25 to 70 ºC increased the aggregation rate. CSC is defined to be a critical value above which the silica dispersion becomes unstable. From experimental observations, Luis Villamizar et al. (2010) reported that pH and salt do not have significant effects on the dispersion stability of nanohybrid particles.

This work is mainly focused on the investigation of silica nanoparticle dispersion stability through several systematic experiments including direct observations, optical absorption measurements, and nanoparticle effective diameter determinations. The stability is investigated in different time intervals. Furthermore, the influences of various parameters like electrolyte concentration, particle diameter, surfactant addition, and temperature on the suspension stability are thoroughly evaluated.

2. Experiment and material

This section briefly discusses the materials used and the experiments performed in this study.

2.1. Materials

a. Nanoparticle: Two kinds of hydrophilic silica nanoparticles with a nominal diameter of 7 and 15 nm were used in this study. They have an unmodified (bare) surface.

b. Surfactants: Two types of surfactants, an anionic and a nonionic surfactant were selected for the experiments. The anionic one is sodium dodecyl sulfate (SDS or NaDS), and the nonionic one is Triton X-100 (C₁₄H₂₉O (C₂H₄O)n) (n=9-10). Both surfactants were purchased from Merck Company.

c. Electrolytes: NaCl and KCl were the inorganic salts used in this work to study the effects of salinity on silica nanoparticle dispersion stability. Additionally, both electrolytes were bought from Merck Company.

d. Aqueous Phase: The aqueous phase used in solution preparation was basically distilled water with the density of 998.2 kg/m³ and the viscosity of 1 cP at the constant temperature of 25 ºC produced in the laboratory. Nanoparticle dispersion and surfactant solutions were prepared by the addition of accurate amounts of relevant material to aqueous phase.

2.2. Nanoparticle solution preparation

Nanoparticle dispersion method is of great importance as the colloidal suspension properties extremely depend on dispersion degree. In this work, we have first wetted nanopowders with a certain amount of distilled water using a magnetic stirrer. Then, particle agglomerates were highly dispersed and deagglomerated using ultrasonic apparatus. It is useful to say that ultrasonic cavitation generates
high shear that breaks particle agglomerates into single dispersed particles. The sonification process was continued for 90 minutes to assure that nanoparticles had been homogenously dispersed. Stock solutions of 0.2 and 2 wt.% were prepared and diluted to the desired concentrations.

2.3. Stability investigation

As mentioned before, several methods were implicated to evaluate the suspension stability at different circumstances. Solutions were observed using a high resolution camera.

In addition, Double Beam Cintra 101 ultraviolet–visible spectrophotometer was used to analyze optical absorbance of silica dispersions. The calculation process of this device is based on Beer-Lambert law. The Beer-Lambert law gives the linear relationship between absorbance and concentration of an absorbing species. The optical absorbance of different nanoparticle dispersions with different concentrations of KCl and NaCl was measured in different periods of time (1 hour, 1 day, 7 days, 10 days, 14 days, and 21 days). The absorbance–time relationship provides a method to study the aggregation of silica dispersions. A schematic of the UV-visible system is shown in Figure 1.

Moreover, a similar procedure was used to determine the effective particle diameter using Scatter Scope 1 Qndix Particle size analyzer.

3. Results and discussion

This section includes the stability evaluation results obtained through various experiments.

3.1. Effect of electrolyte concentration on the stability of nanoparticle dispersions

Figure 2 shows the phase behavior of 0.05 wt.% silica dispersion in different NaCl concentrations. It can be seen that the addition of NaCl up to around 3 wt.% does not destabilize the dispersion of silica nanoparticles after 21 days. Above this critical concentration, a further increase in NaCl concentration leads to dispersion instability. Therefore, an approximate value of 3 wt.% is defined as the CSC for NaCl. This behavior can be explained by DLVO theory. According to this theory, electrostatic forces are highly dependent on electrolyte concentration in dispersion. As the electrolyte concentration increases, the thickness of the diffuse electrical layer decreases and particles tend to aggregate. This declines the repulsive forces between particles. Because the repulsive forces prevent the aggregation of particles, large electrolyte concentration allows the attractive van der Waals forces to dominate, and particles tend to aggregate.
Figure 2
Phase behavior of 0.05 wt.% silica nanoparticle dispersions at various NaCl concentrations in different days.

It must be mentioned that CSC is also dependent on nanoparticle concentration. As the particle concentration increases from 0.05 wt.% to 0.1 wt.%, the CSC decreases to 2 wt.%. The results are shown in Figure 3.

Figure 3
Phase behavior of 0.1 wt.% silica nanoparticle dispersions at various NaCl concentrations in different days.
According to Metin et al. (2010) three distinct stages of aggregation occur in the presence of salt: clear dispersed, turbid, and two separated phases. However, the aggregation of nanoparticles may not be visually observed at early stages. CSC may be determined accurately through the measurements of optical absorption and effective diameter of silica nanoparticles in different periods of time. Figure 4 shows the optical absorbance at 390-nm wavelength for 0.05 wt.% particle dispersion in the presence of NaCl. The CSC, determined at a point of sharp change in the absorbance profiles shown in Figure 4, is 4 wt.% after 10 days. As is presented in Figure 5, this value decreases to 2 wt.% as the nanoparticle concentration increases to 0.1 wt.% These values are consistent with the ones obtained through direct observations. From Figures 4 and 5, it can be inferred that the CSC is a function of time. For example, it reduces from 3 wt.% at 3 days to 2 wt.% after 14 days (Figure 5).

**Figure 4**
UV-Visible absorbance of 0.05 wt.% silica dispersion in different day at 390-nm wave length at 25 °C.

**Figure 5**
UV-Visible absorbance of 0.1 wt.% silica dispersion in different day at 390-nm wave length at 25 °C.
Figures 6 and 7 show the results of effective particle diameter measurements for different NaCl and nanoparticle concentrations in different periods of time. The profiles of effective particle diameters are quite similar to optical absorbance profiles. As it is seen in Figure 6, the increase in NaCl concentration to 3 wt.% has sharply increased the size of nanoparticles from 74 to 462 nm after 14 days. Furthermore, as the nanoparticle concentration increase to 0.1 wt.% (shown in Figure 7), a sudden increase in the size of nanoparticle was observed at lower concentrations of NaCl for each period of time. For example, CSC reduced to 2 wt.% after 14 days. As it was mentioned in the previous paragraph, this value is 3 wt.% for 0.05 wt.% nanoparticle concentration.

**Figure 6**
Effective particle diameter of 0.05 wt.% silica dispersions in the presence of NaCl.

**Figure 7**
Effective particle diameter of 0.1 wt.% silica dispersions in the presence of NaCl.
3.2. Effect of ionic strength on the stability of nanoparticle dispersions

Figure 8 shows the phase behavior of 0.05 wt.% silica dispersion in different KCl concentrations. It can be seen that the CSC for KCl is less than that for NaCl. According to the DLVO theory, the diffuse electrical layer of charged particles in dispersions is compressed at higher ionic strength, and thus the repulsive potential of the particles reduces. The thickness of diffuse electrical layer is calculated from the following theoretical equation (Hunter, 2001):

\[
\kappa^{-1} = \frac{1}{3.288\sqrt{I}} \text{ (nm)}
\]  

(1)

where, \( I \) is the ionic strength. According to the above equation, as ionic strength of KCl is more than NaCl, the thickness of its electrical layer is less and eventually the silica dispersion becomes unstable at lower concentrations of this electrolyte compared to NaCl.

![Figure 8](image)

**Figure 8**
Phase behavior of 0.05 wt.% silica nanoparticle dispersions at various KCl concentrations in different days.

The optical absorbance and effective particle diameter for 0.05 wt.% in different KCl concentrations were determined at different time intervals to calculate the CSC more accurately. The results are given in Figures 9 and 10. A significant increase in optical absorbance of particles occurs at 1 wt.% (CSC) of KCl after 14 days (Figure 9), while this value is 3 wt.% for NaCl as shown in Figure 6. As it is clear, the results of particle diameters measurement shown in Figure 11 are identical as optical absorbance determination. A sharp increase can be seen while KCl concentration is above 1 wt.% after 14 days.
Figure 9
UV-Visible absorbance of 0.05 wt.% silica dispersion in different day at 390-nm wavelength at 25 °C.

Figure 10
Effective particle diameter of 0.05 wt.% silica dispersions in the presence of KCl.

3.3. Effect of nanoparticles size on the stability of nanoparticle dispersions
In order to investigate the effect of nanoparticle size on dispersion stability, two types of nanoparticles with nominal diameters of 7 and 15 nm were used. The obtained results are presented in Figure 11. The experimental studies have revealed that, at low electrolyte concentrations, the nanoparticles tend to aggregate more as the size of particles increases, and, at high electrolyte concentrations, the greater the size of nanoparticles is, the more unstable the suspensions would be (Bargozin 2012). At high electrolyte concentrations, ions existing in the dispersion cover the nanoparticles and neutralize the charge of their surface. In this condition, the effect of the diffuse electrical layer is negligible and it allows the attractive van der Waals forces to dominate, and silica particles aggregation and sedimentation occur. The results showed that CSC decreased sharply from 3 wt.% to 0.5 wt.% NaCl after 21 days as the size of nanoparticles increased to 15 nm. Figure 12 presents the optical
absorbance of silica nanoparticle dispersions of 15 nm diameter as a function of NaCl concentration. The optical absorbance of particle suspension increases suddenly with NaCl concentrations above 0.5 wt.% (CSC) after 10 days.

**Figure 1**
Phase behavior of 0.05 wt % silica nanoparticle (15 nm) dispersions at various NaCl concentrations in different days.

**Figure 12**
UV-Visible absorbance of 0.05 wt.% silica dispersion (15 nm) in different day at 390-nm wave length at 25 °C.
3.4. Effect of temperature on the stability of nanoparticle dispersions

To investigate the temperature effect on nanoparticle suspensions stability, dispersions of different NaCl and KCl concentrations were maintained at temperatures of 50, 70, and 90 °C. The results shown in Figures 13 and 14 indicate that the CSC is significantly reduced as temperature increases. In other words, at higher temperatures, particle collision rate is increased and the aggregation and instability occurs at lower salt concentrations. Figure 11 presents the phase behavior of 0.05 wt.% of silica dispersion in the presence of NaCl and KCl at 70 °C.

Figure 13
Effect of temperature on CSC of NaCl.

Figure 14
Effect of temperature on CSC of KCl.
3.5. Stability of silica nanoparticle dispersions in the presence of surfactant

Figures 16 and 17 show the effect of two kinds of surfactant on the stability of the silica nanoparticle dispersions. The results have revealed that, in the presence of anionic surfactant (SDS), particle dispersions are more stable at high electrolyte concentrations (CSC is higher), while nonionic surfactant (TX-100) causes dispersion instability. For example, CSC for NaCl increases to 5 wt.% when SDS surfactant with a constant concentration of 0.1 wt.% is used (see Figure 16). On the other hand, instability was observed in nanoparticle dispersions at a low concentration of NaCl in the presence of TX-100 as shown in Figure 17. Most often, electrical double layers are observed on the interface between a solid body (e.g. silica nanoparticle) and an electrolyte. This layer helps the anionic surfactant to approach and cover the surface of nanoparticles that have negative charges. Then, the hydrophobic tails of surfactant generate a steric repulsive force and prevent the nanoparticle aggregation, and dispersion remains stable. But in the case of nonionic surfactants, there are no effective forces to approach them to nanoparticle surfaces and thus the dispersion tends to be unstable even at very low electrolyte concentrations. The results are summarized in Table 1.

![Figure 15](image1.png)

**Figure 15**
Phase behavior of silica dispersion in the presence of NaCl and KCl at 70 °C; a) after 1 hr; and b) after 21 days at 70 °C.

![Figure 16](image2.png)

**Figure 16**
Effect of SDS (1000 ppm) on stability of nanoparticle dispersion in different NaCl concentration at 60 °C; a) after 1 hr; and b) after 21 days.

![Figure 17](image3.png)

**Figure 17**
Effect of TX-100 (1000 ppm) on stability of nanoparticle dispersion at different NaCl concentrations at 60 °C; a) after 1 hr (stable condition); and b) after 2 hr (unstable condition).
Table 1
Surfactants effect on CSC.

<table>
<thead>
<tr>
<th>Electrolyte type</th>
<th>CSC after 21 day wt%</th>
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<tbody>
<tr>
<td></td>
<td>Without surfactant</td>
</tr>
<tr>
<td>NaCl</td>
<td>3</td>
</tr>
<tr>
<td>KCl</td>
<td>1</td>
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4. Conclusions

In this study, the effects of different parameters such as electrolyte concentration and temperature on the stability of silica nanoparticle dispersions were experimentally investigated. The results have shown that dispersions of higher nanoparticle concentrations were more severely exposed to destabilization after the inclusion of electrolytes. It was also observed that nanoparticle dispersion stability could not be retained beyond a certain electrolyte concentration, called critical salt concentration (CSC). CSC was strongly influenced by the electrolyte type, particle concentration and size, temperature, and surfactant addition. It was revealed that the CSC of KCl was much lower than that of NaCl due to its higher ionic strength. Additionally, the CSC value was greater for nanoparticles with smaller diameters. It was shown that the increase in temperature might cause the instability of nanoparticle dispersions and that it significantly reduces the CSC amount. Finally, the dispersion stability was improved with the addition of anionic surfactant, whereas no positive influence was observed for the nonionic one.

In this study, the influences of different parameters on the stability of hydrophilic silica nanoparticles were considered. Similar surveys can be performed to investigate the effects of such parameters on the stability of other types of silica nanoparticles (such as hydrophobic). Furthermore, the stability of silica nanoparticles in the presence of divalent electrolytes (e.g., MgCl$_2$) can also be studied.

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Nomenclatures

<table>
<thead>
<tr>
<th>CSC</th>
<th>Critical salt concentration</th>
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<tr>
<td>EOR</td>
<td>Enhanced oil recovery</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
</tr>
<tr>
<td>Tx-100</td>
<td>Triton x-100</td>
</tr>
</tbody>
</table>

References

Ayatollahi, Sh. and Zerafat, M., Nanotechnology-assisted EOR Techniques: New Solutions to Old Challenges, Paper SPE 157094 Presented at the SPE International Oilfield Nanotechnology


