Adsorption of Functionalized Silica Nanoparticles on Swelling Clay Minerals

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ABSTRACT

Successful application of nanoparticles is dependent on understanding the mobility, retention, and transport fate of nanoparticles in natural formations. These aspects are greatly influenced by subsurface environmental conditions such as electrolyte type and concentration, temperature, pH and mineral composition of the formation as well as characteristics of the nanoparticle itself such as concentration and surface modifications. Characterizing the effects of surface functionalization and retention of nanoparticles onto clay minerals due to adsorption under subsurface conditions will be necessary for selecting the types of nanoparticles or surface modification to be used as suitable nanosensors or EOR agents. In this study, the effects of surface functionalization through a polyethylene (PEG) coating on 5 nm silica nanoparticle on mobility was evaluated through observations on clay swelling inhibition. Adsorption onto montmorillonite and illite was also investigated. Visual swelling tests were utilized to investigate clay swelling inhibition and ultraviolet-visible (UV-vis) spectroscopy was used to determine the concentration of adsorbed nanoparticles in conditions that are likely to be found in subsurface reservoir environments.

Keywords: nanoparticle, clay, swelling, polyethylene glycol

1 INTRODUCTION

There is great interest in identifying and investigating agents that reduce the degree of clay swelling. Polyols, such as glycols and glycerols, and recently amine based compounds have been established as effective shale inhibitors for the prevention of wellbore instability [1-4]. With regards to adsorption, Metin et al. [5] studied the adsorption of both unmodified and surface functionalized (PEG- or sulfonate-modified) silica nanoparticles onto calcite and quartz surfaces. The results suggest that adsorption did not occur between both unmodified and surface functionalized nanoparticles with the minerals studied. Yu et al. [6] conducted a study on the adsorption and transportation behavior of silica nanoparticles in three different porous media and small amounts of nanoparticles were observed to adsorb onto the sandstone and limestone cores while no adsorption was observed for dolomite.

In our previous work, we characterized the effects of a polyethylene glycol (PEG) coating on the transport and the aqueous stability of silica nanoparticles under conditions that are likely to be encountered in subsurface environments [7]. Nanoparticle mobility was evaluated by studying the effects of electrolyte type (NaCl, KCl) and concentration, nanoparticle concentration, pH, and temperature on the inhibition of clay swelling.

In this study, we attempt to relate the effects of surface functionalization through a polyethylene (PEG) coating on 5 nm silica nanoparticle on clay swelling inhibition with nanoparticle adsorption onto clay minerals, specifically montmorillonite and illite. Visual swelling tests were utilized to investigate clay swelling inhibition and ultraviolet-visible (UV-vis) spectroscopy was used to determine the concentration of adsorbed nanoparticles in conditions that are likely to be found in subsurface reservoir environments.

2 MATERIALS AND METHODS

The montmorillonite and illite clay was purchased from Ward's Natural Science Establishment, Inc. and dry sieved through 400 and 200 mesh sieves to obtain particle sizes between 38 and 74 μm, respectively. The clays were then dried at 110 ℃ overnight and stored in a desiccator jar prior to use. No further purification of the clay was performed. The batch adsorption experiments were prepared by adding 0.05 g of the clay to each of the glass vials. The adsorption experiments were performed in the presence of 1.5 wt% NaCl as a background electrolyte to decrease the amount of dispersed clay in solution and to decrease the degree of clay swelling for more accurate absorbance readings. After the addition of the brine to the clay, the samples were left undisturbed for two days to allow the clay particles to settle. The absorbance readings of the supernatent was performed using a Cary 50 ultraviolet-visible spectrophotometer (UV-vis) to confirm that there were no clay particles dispersed in the solution. NaCl and KCl solutions were also confirmed to lack absorbance readings in the ultraviolet regions studied. A stock solution containing 21.2% polyethylene (PEG) coated silica nanoparticles provided by 3M was carefully added to the clay-brine solution without dispersing the clay particles in the sediment. The silica nanoparticle dispersions were added to achieve initial concentrations of 0.5, 1, 1.5, 2, 3,

and 5 wt%. The samples were left undisturbed for ten days to allow for equilibration. The absorbance at 300 nm was recorded for nanoparticle dispersions of known concentrations to produce a calibration curve, which was then used to estimate the nanoparticle concentration at equilibrium. The adsorption isotherm curves were generated by using the following equation to determine the adsorbed amounts, a (g/g clay):

$$a = 0.01(c_i - c_e)M \cdot m^{-1}$$

where $c_i - c_e$ represents the difference in initial and equilibrium concentrations (wt%), M is the mass of the nanoparticle dispersion, and m is the mass of the clay (adsorbent).

The protocol for visual swelling tests was adapted from American Society for Testing and Materials (ASTM)'s D5890-11 protocol. 0.1 g of montmorillonite was dispersed in previously prepared nanoparticle dispersions to obtain 5 g in total weight and sealed in glass vials. A stock solution containing 21.2% by weight 5 nm PEG-coated silica nanoparticles was diluted with deionized water to the desired concentration.

3   RESULTS AND DISCUSSION

3.1   Adsorption

The adsorption isotherm of nanoparticles onto illite is presented in Figure 1. The adsorption of nanoparticles onto illite is much lower compared to montmorillonite. It is not surprising that adsorption occurred since illite has a crystal structure layering pattern similar to montmorillonite, except the interlayer sheets are held together by a potassium atom. Compared to montmorillonite, illite is considered a non-swelling clay due to the presence of K+ cations in the hexagonal holes in the silica sheet which strongly bonds the layers together [8]. The decreased spacing of the interlayer region limits movement and entry of the nanoparticles into the interlayer region in much the same way KCl acts on montmorillonite to decrease nanoparticle adsorption.

Adsorbed amounts of nanoparticles onto the clays surfaces did not display saturation under the conditions studied. Figure 2 presents the adsorption isotherms of silica nanoparticles in g/g clay at equilibrium concentrations in the presence of 1.5 and 3 wt% NaCl background concentrations. At up to 1 wt% nanoparticle concentrations, there is no significant difference in adsorption between 1.5 and 3 wt% background NaCl concentrations. Exceeding this nanoparticle concentration yields noticeably lower adsorbed amounts for 3 wt% NaCl adsorption isotherm. A recent study by Metin et al. demonstrated that the PEG-coated silica nanoparticle dispersion remains stable at NaCl concentrations up to 10 wt%, suggesting that the observed decreased adsorption at a higher NaCl concentration is unlikely due to homo-aggregation of the nanoparticles [9].

Figure 3 shows that adsorption isotherm for KCl is lower compared to NaCl at the same concentration for all equilibrium nanoparticle concentrations. The adsorbed amount appears to be dependent on the magnitude of clay swelling influenced by the concentration and type of electrolyte at 25 ºC. As electrolyte concentration increases, the magnitude of clay swelling is reduced in visual observation studies. The crystal lattice of the clay is able to exchange cations within a solution to neutralize the charge deficiency of the clay, influencing the degree of clay swelling. KCl is known to decrease the magnitude of clay swelling. The ionic radius of the K+ cation approximates the hexagonal holes in the silica sheet of the clay, and is able to situate within the cavity. The immobilized K+ cations on either side of the interlayer space are able to share a water molecule in this region and to reduce clay swelling [8].

3.2   Clay Swelling

Montmorillonite is widely known to display decreased swelling potential in the presence of brine solutions such as NaCl and KCl. The macroscopic swelling of montmorillonite was visually observed in the presence of varying electrolyte types and concentrations. The effect of NaCl on clay swelling in the absence of nanoparticles is shown in Figure 4(a). The concentration of NaCl is increased from 0.5 wt% to 5 wt% as is shown from left to right. As NaCl concentration increases, the volume of the clay sediment decreases. The same procedure was repeated in the presence of KCl and a similar trend was observed. However, the magnitude of clay swelling was considerably lower in the presence of KCl compared to NaCl. This inhibition of clay swelling is thought to be due to the ability of KCl to compress the electrical double layer and decrease the electrostatic repulsion between the clay particles [10]. Liu and Lu proposed that osmotic swelling in K-montmorillonite is inhibited energetically when the water content is higher than the range of the double-layer hydrate [11]. Their study suggests that Na-smectites prefer expanded states (double layer, triple layer, and fully expanded) to a single-layer hydrate, while K-smectites prefer the single-layer state over the double-layer state. The K+ cations form coordinate structures with the oxygen atoms of the hexagonal ring situated on the clay surface and are effectively immobilized. The fixed K+ cations on either side of the interlayer space are able to share a water molecule in this region. The neutralization of the negative clay surface charge by K+ cations inhibits further swelling.

Montmorillonite exposed to a series of solutions containing only nanoparticles in the absence of electrolytes resulted in a turbid mixture lacking a well-defined boundary between the clay mineral and aqueous solution. Addition of 5 nm PEG-coated silica nanoparticles to achieve 0.5 wt% in the presence of the brine solution is shown in Figure 4(b). When nanoparticles are present, a reduction in the magnitude of clay swelling was observed for all salt

concentrations relative to dispersions containing NaCl only. The increasing nanoparticle concentration, as shown in Figure 4, corresponds to a decrease in the magnitude of clay swelling.
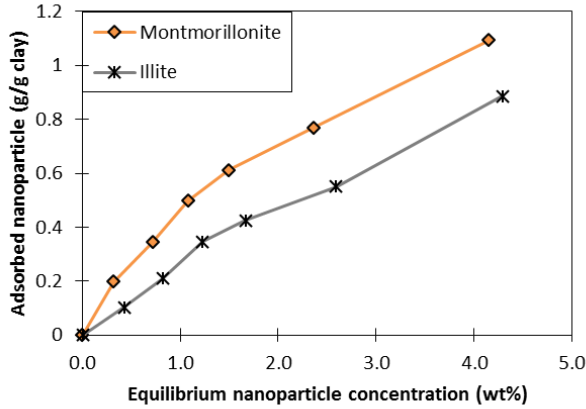

Figure 1- Isotherms for the adsorption of nanoparticles on montmorillonite and illite at in the presence of 1.5 wt% NaCl at 25 °C
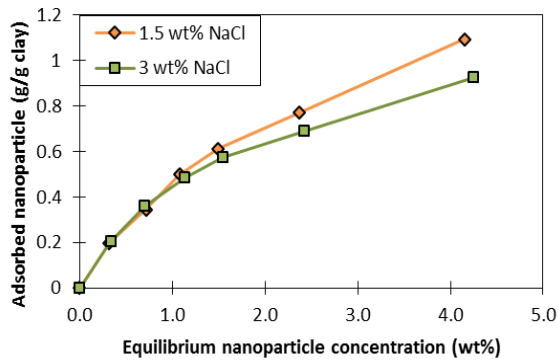

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Figure 2- Isotherms for the adsorption of nanoparticles on montmorillonite at 1.5 and 3 wt% NaCl concentrations at 25 °C
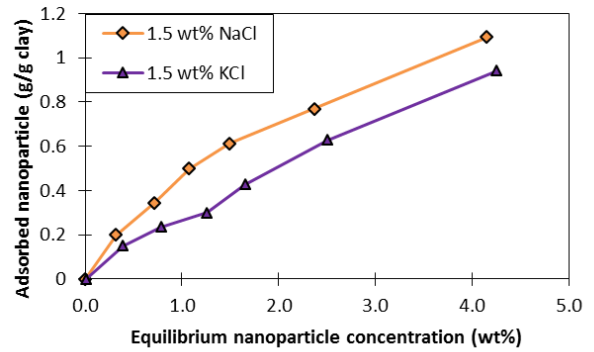

Figure 3- Isotherms for the adsorption of nanoparticles on montmorillonite at 1.5 wt% NaCl and 1.5 wt% KCl concentrations at 25 °C

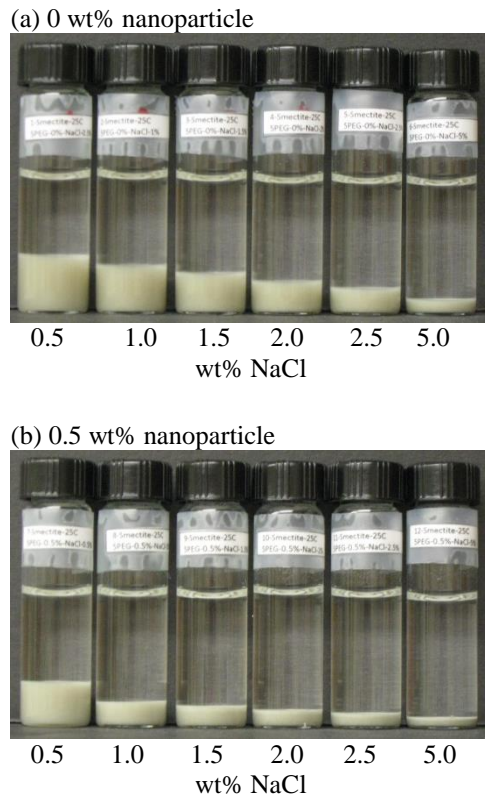(a) 0 wt% nanoparticle

(b) 0.5 wt% nanoparticle

Figure 4- Photographs of sealed glass vials containing 0.1 g of montmorillonite in the presence of NaCl with (a) deionized water only, (b) 0.5 wt% nanoparticle concentrations

4   CONCLUSIONS

Adsorption isotherms for illite indicate significant decreases in adsorption. The non-swelling nature of the clay

and presence of potassium atoms in the interlayer sheets is thought to restrict nanoparticle movement into interlayer region, similar to the ability of KCl to reduce the interlayer spacing in montmorillonite.

We observed significant amounts of adsorption for PEG coated silica nanoparticles onto montomorillonite and illite surfaces in our experiments. Nanoparticle adsorption was found to be influenced by the availability of clay surface area for binding and a relationship between the magnitude of clay swelling and adsorbed amounts of nanoparticles was observed. The presence of electrolytes such as NaCl and KCl is known to reduce the spacing between the interlayer sheets. As NaCl concentration increased, a reduction in nanoparticle adsorption was observed. KCl is known to reduce the interlayer spacing and swelling more than NaCl, and our results demonstrate decreased nanoparticle adsorption in the presence of KCl. Saturation of nanoparticle adsorption was not observed under the conditions studied, although the adsorption isotherm curves suggests increased difficulty in binding as nanoparticle concentration increased.

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