

Interaction of Surface Modified Silica Nanoparticles with Clay Minerals

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ABSTRACT

The interaction of silica nanoparticles with montmorillonite clay was investigated by visual swelling tests and analytical techniques such as Fourier Transform Infrared (FTIR) and x-ray diffraction (XRD). The adsorption of silica nanoparticles onto montmorillonite was also studied with a UV-Vis spectrophotometer. The effects of particle size, concentration, and surface type on the adsorption were presented in detail. Silica nanoparticles with four different surfaces (unmodified, surface modified with anionic (sulfonate), cationic (quaternary ammonium (quat)), or nonionic (polyethylene glycol (PEG)) surfactant) were used. The adsorption of unmodified and sulfonate modified nanoparticles on clay was insignificant. However, PEG and quat/PEG modified nanoparticles adsorbed significantly on montmorillonite. Adsorption isotherms were calculated for those nanoparticles. Additionally, it does not appear that the particle size significantly influences the extent of adsorption.

Keywords: surface modified silica nanoparticles, adsorption on clay minerals, sulfonate, quaternary ammonium, polyethylene glycol

1 INTRODUCTION

Most hydrocarbon bearing sandstone reservoir rocks contain clay minerals in which kaolinite, montmorillonite, illite, and chlorite are abundant. Clay swelling has been an active area of research. Especially in drilling and hydrocarbon production engineering, clay swelling has significant impacts such as wellbore instability and hydrocarbon formation damage. The mechanisms for clay swelling are well defined. However, there is very little work published on the interactions of engineered nanoparticles with clays and the mechanisms are not well understood.

The basic structure of clay minerals consists of a sheet of oxygen or hydroxyl groups embedding heavy metals such as aluminum, iron, or magnesium atoms, and a sheet of silica tetrahedral. Two sheets of silica sandwiching on one sheet of aluminum defines a basic layer of montmorillonite. These layers are separated by thin aqueous films that contain cations and organic materials [1]. This particular structure of montmorillonite is mainly responsible for the expansion of montmorillonite in the

presence of water. Clay swelling has been an active area of research since 1950s. Especially in drilling and production engineering, clay swelling has significant impacts such as wellbore instability and formation damage.

The mechanisms and kinetics of clay swelling in petroleum-bearing formations was discussed in detail by Civan [2]. Sensoy et al.[3] reported that nanoparticles at 10 wt% or higher concentrations could plug shale pore throats and reduce permeability to minimize fluid invasion. Cai et al. [4] argued that the use of nanoparticles in drilling fluids would be the first large scale application of nanotechnology in the oil and gas industry. The authors showed experimentally that unmodified nanoparticles could reduce the invasion of water-based drilling fluids into shale.

This study brings new insight into the understanding and modeling of the adsorption of surface modified silica nanoparticles onto clay minerals.

2 MATERIALS AND METHODS

The materials studied were aqueous dispersions of silica particles as provided by 3M, Co (St. Paul, MN, USA). The mean diameters of primary particles are 5 and 25, which have an unmodified surface or a modified surface with sulfonate, polyethylene glycol (PEG) or a mixture of quaternary ammonium and PEG. The latter one will be referred to as “quat/PEG” throughout this chapter. The surface modifications describe the surface of the particles after using alkoxysilanes as surface modifying agents. We used montmorillonite clay purchased from Ward’s Natural Science Establishment, Inc. for these studies. Throughout this chapter montmorillonite is referred as “clay”. An ultraviolet-visible spectrophotometer (UV-Vis) was used to determine the concentration of nanoparticles in the supernatant liquid.

Powder of montmorillonite clay mineral was submerged in the various nanoparticle dispersions for 24 hours. The liquid of an amount of 3 ml was separated from the mineral by pipette and centrifuge. The supernatant liquid was centrifuged 15 minutes at 9,000 rpm to separate fine clay minerals from the liquid and then analyzed by UV-Vis spectroscopy to determine the silica nanoparticle concentration remaining in the liquid. A calibration curve was built using UV-Vis absorbance at a fixed wavelength as a function of nanoparticle concentration. Different nanoparticle concentrations were used ranging from 0.04 to

6 wt%. The dispersion to mineral weight ratio was 100:1. This liquid-to-solid ratio was chosen based on the extent of the swelling of clay in water that would give enough supernatant for concentration measurements.

3 RESULTS AND DISCUSSION

First, the effect of nanoparticles on swelling of montmorillonite clay was studied by visual observations by adding 0.2 g of clay to 10 g of aqueous nanoparticle dispersion. It is known that there are two types of swelling mechanisms depending on the extent of the increase in the basal spacing between two montmorillonite sheets: crystalline and osmotic swelling. Crystalline swelling results from the adsorption of the monomolecular layers of water on both the external and interlayer surfaces. In osmotic swelling, the interlayer spacing increases abruptly to 30-40 Å and continues to increase to several hundred angstroms (several ten nanometers) with water content [5]. In the presence of electrolytes, the swelling of clay is suppressed. As NaCl concentration increases, the volume of the clay sediment decreases. It is known that K⁺ is more effective in inhibiting clay swelling than Na⁺. In the presence of unmodified nanoparticles, the clay swelling is similar to that without any nanoparticles. At a low nanoparticle concentration (~1 wt%), all the nanoparticles (unmodified or modified) show slightly larger sediment volume than that without any nanoparticles. However, as nanoparticle concentration increases, PEG and quat/PEG modified nanoparticles inhibit swelling and the sediment thickness is smaller than that without any nanoparticles. Figure 1 clearly illustrates the effect of nanoparticle concentration on clay swelling. Sulfonate modified or unmodified nanoparticles do not show any effect on clay swelling. However, PEG or quat/PEG modified nanoparticles inhibit clay swelling and as nanoparticle concentration increases, the clay swelling becomes less significant. For unmodified and sulfonate modified nanoparticle, we did not observe any improved inhibition of clay swelling. However, the presence of PEG or quat/PEG modified nanoparticles decreased the degree of swelling as indicated by the level of sediment height.

We studied the adsorption of unmodified and modified nanoparticles on clay with a UV-Vis spectrophotometer. We did not observe any significant adsorption with 5 nm unmodified or sulfonate modified silica nanoparticles. This result is in agreement with the visual observations on clay swelling as presented above. However, PEG or quat/PEG modified nanoparticles showed significant adsorption on clay. A background electrolyte of 1.5 wt% NaCl was chosen to decrease the amount of dispersed clay in solution and decrease the degree of swelling so that we could relate the results for possible oil field applications.

The UV-Vis absorbance spectra for 5 nm PEG modified nanoparticle dispersions is shown in Figure 2 before and after the dispersion was in contact with clay. The results of

adsorption are shown in Figure 3 for both 5 and 25 nm PEG modified nanoparticles. The effect of particle size seems to be negligible on adsorption. Figure 4 presents the adsorption isotherm for PEG and quat/PEG modified 5 nm nanoparticles. We observed that PEG or quat/PEG modified silica nanoparticles have a strong affinity for the clay as indicated by the shapes of the isotherms. The effect of cation type was also studied. The results showed that the extent of adsorption of 5 nm PEG modified silica nanoparticles decreased when K⁺ was present. We have shown by visual observations that PEG modified nanoparticles were more effective in clay inhibition in the presence of K⁺ than Na⁺.

In addition to the above discussion on the interaction of PEG and clay in the presence of K⁺ and Na⁺, Parfitt and Greenland [6] suggested that the direct interaction between the exchangeable cations and PEG molecules was not responsible for adsorption (ion-dipole interactions). Instead, it was proposed that the cations retained their hydration shell and that weak bonds were involved between the primary hydration shell of the exchangeable cation and that of the ether oxygen atoms of the polymer to give a water bridge. Burchill et al. [7] demonstrated through neutron scattering studies that hydrophilic polymers were able to displace the non-coordinated water and bind to the silicate surface as well as to the exchangeable cations through water bridge mechanism. The adsorption of PEO onto Na-montmorillonite gave Langmuir type isotherms and the adsorbed amount increased with the molecular weight. Cliffe et al. [8] showed that the adsorption of PEG onto Na-montmorillonite gave Langmuir type isotherms without reaching a plateau. We have presented similar adsorption behavior for PEG or quat/PEG modified nanoparticles on clay in Figure 3-4. In these figures, the adsorption results are also presented in terms of a fraction of a monolayer surface coverage of nanoparticles on clay mineral. Assuming a cubic packing of nanoparticles on clay surface, 4×10^{16} and 1.6×10^{15} nanoparticles of 5 and 25 nm diameter respectively can pack on 1 m² surface area of clay. The specific surface area of clay used in calculations is 560 m²/g [9]. It is observed that for larger nanoparticles (25 nm) the surface coverage on clay is much smaller than with 5 nm nanoparticles (see Figure 3). This suggests that 25 nm particles have more sparse packing on the clay surface as compared to 5 nm particles.



Figure 1: Picture of 10 g solution of DI water, 1, 5, and 10 wt% 5 nm PEG modified nanoparticle dispersions. Each sample contains 0.2 g clay and there is no background NaCl in the solution. The picture was taken 4 months after preparation of samples.

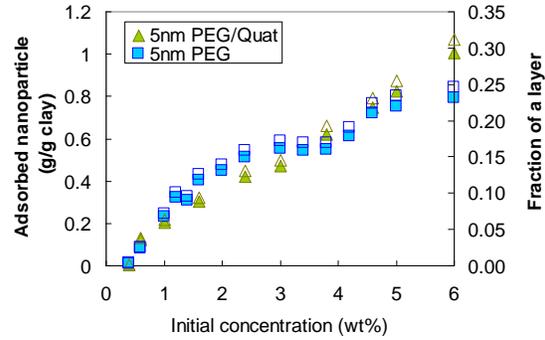


Figure 4: Adsorption of PEG or quat/PEG modified silica nanoparticles on clay at 1.5wt% NaCl solution. The data with open symbols correspond to the secondary y-axis of fraction of a layer.

4 CONCLUSIONS

It is concluded that unmodified or sulfonate modified silica nanoparticles do not have any effect on clay swelling. However, PEG modified or quat/PEG modified silica nanoparticles decrease the extent of clay swelling. The presence of K^+ improves the effectiveness of the inhibition of clay swelling by these nanoparticles.

The adsorption of unmodified and sulfonate modified nanoparticles on clay was found to be insignificant. However, PEG and quat/PEG modified nanoparticles adsorbed significantly on montmorillonite. Adsorption isotherms were calculated for those nanoparticles. Additionally it does not appear that the particle size significantly influences the extent of adsorption. The size of the nanoparticles affects the surface coverage of nanoparticles on clay. The adsorption isotherms do not level off at the concentration range of nanoparticles studied.

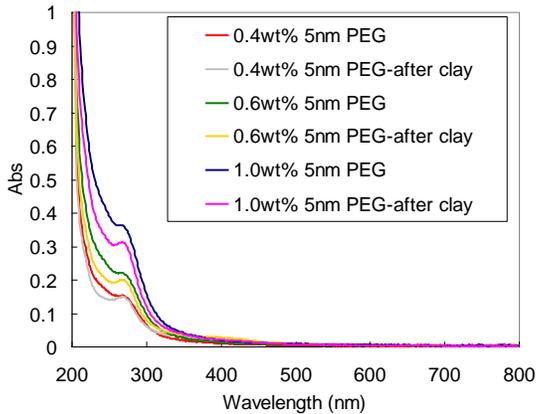


Figure 2: UV-Vis spectra for 5 nm PEG modified silica nanoparticle dispersions before and after in contact with clay.

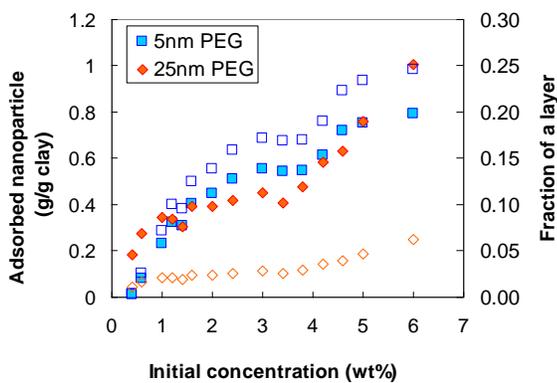


Figure 3: Adsorption of PEG modified silica nanoparticles on clay at 1.5wt% NaCl solution. The data with open symbols correspond to the secondary y-axis of fraction of a layer.

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