The Retention of Silica Nanoparticles at Oil/Water Interface

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ABSTRACT

The retention of silica nanoparticles at water/crude oil interface is studied in this paper. Silica nanoparticles with two different surfaces (unmodified, surface modified with nonionic (PEG) surfactant) are used. Interfacial tension (IFT) measurements provide us the means to investigate the adsorption of silica nanoparticles at the crude oil/water interface. Unmodified nanoparticles do not change the IFT of crude oil/water interface. However, the presence of sulfonate or PEG modified nanoparticles in solution lower the IFT. We also carried out flow experiments with PEG modified silica nanoparticles through a glass bead pack. In the absence of crude oil, the nanoparticles act like a conservative tracer with insignificant interaction with the glass beads. This result is in agreement with our previous work on the adsorption of silica nanoparticles on mineral surfaces. However, at the residual oil saturation of 12%, PEG modified silica nanoparticles are retained at crude oil/water interface, as shown by the concentration profile. These results are also in agreement with IFT and the contact angle measurements carried out in this study.

Keywords: interfacial tension, silica nanoparticles, surface modified nanoparticles, adsorption at oil/water interface, flow through permeab media

1 INTRODUCTION

The interaction of nanoparticles with liquids (water/oil interface) or solids (mineral surfaces) determines the mechanisms of retention of nanoparticles in reservoir rocks. Previously, we investigated the adsorption of silica nanoparticles onto quartz and calcite surfaces and at the decane/water interface [1]. Insignificant adsorption of unmodified, sulfonate or PEG modified silica nanoparticles on quartz and calcite surface was observed. The type and amount of surface treatment attached to silica nanoparticles determined the extent of the change in interfacial tension (IFT) of decane/water interface [1]. Similarly, Lee et al. [2] observed that the modification methods and chain length of modifying agents on silica nanoparticles determined the structure of particle layering at the air/water interface in the presence of a cationic surfactant. Binks and Whitby [3] studied the effect of precipitated silica nanoparticles on stabilizing oil-in-water emulsions. The emulsion stability was controlled by changing the pH or particle charge. The authors observed that adding cationic surfactants improved the emulsion stability. A comprehensive literature review on nanoparticles at fluid interfaces was presented by Bresme and Oettel [4].

In this work, we investigate the retention of silica nanoparticles at water/crude oil interface. Silica nanoparticles with two different surfaces (unmodified, surface modified with nonionic (PEG) surfactant) are used. Interfacial tension (IFT) measurements provide us the means to investigate the adsorption of silica nanoparticles at the crude oil/water interface. The effect of pH was investigated with IFT. The flow of nanoparticles in glass bead packs was also studied in the presence of residual oil.

2 MATERIALS AND METHODS

Interfacial tensions were measured with a Rame-Hart surface tension instrument by using pendant drop method [5]. An oil droplet was formed at the end of a J-needle in an optical glass cell filled with 100 ml of aqueous solution (water or nanoparticle dispersion). Then the drop was imaged with a video camera. The interfacial tension was calculated using DROPimage software [6] by analyzing the shape of the drop. On the basis of the Young-Laplace equation describing the drop profile of pendant, DROPimage software calculated the surface tension from digitized picture data [6]. The oil used in this study was Yates crude oil.

The flow experiments were conducted in the flow loop. The permeable media used in this section was composed of 100-140 mesh size glass beads purchased from Potters Industry Inc. The glass beads were cleaned with distilled water, dried in an oven set at 100 $^{\circ}$C for a couple of days and sieved using several meshes stacked on top of each other, ranging from 40 to 170, for 20 minutes under the agitation of a Ro-Tap sieve shaker. The grains collected at 100-140 mesh were used to pack the glass column. A flow adapter and glass column of 2.5 cm diameter and 30 cm long were purchased from Kimble Chase for the preparation of the glass bead pack. Glass columns of 4.8 cm diameter by Kimble Chase were used to store the fluid to be injected. An Isco pump delivered mineral oil to the glass column displacing the injected fluid to the permeable media. The pressure drop across the permeable media was measured with differential pressure transducers connected in parallel to the inlet and outlet. Low (0-1 psid) and high range (0-10 psid) transducers were purchased from Cole-Parmer and Rosemount Inc. respectively. A bleeding line was connected to the pressure transducer to displace any air bubbles trapped in the tubes before each experiment started. The effluent was collected in a fraction collector in 15 ml

plastic centrifuge tubes. A schematic presentation of the flow loop is presented in Figure 1. The porosity and permeability were determined as 40.3% and 7 D. The concentration of nanoparticles in the effluent was determined using a conductivity probe and a UV-Vis spectrophotometer.
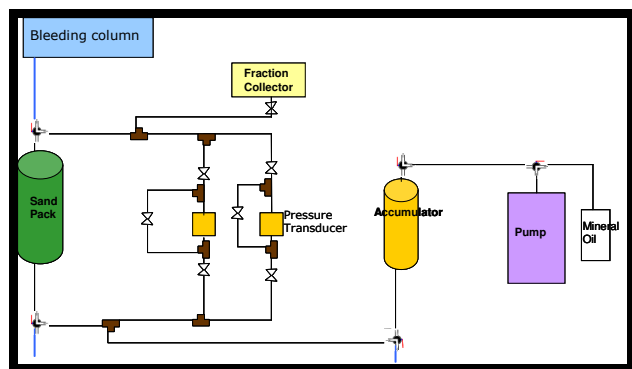

Figure 1- The schematic presentation of the flow loop.

3 RESULTS AND DISCUSSION

The interaction between nanoparticles and crude oil was investigated by interfacial tension (IFT) measurements. Figure 2 presents the pictures of the oil droplet and how its shape changes as the PEG modified nanoparticle concentration changes. The change in IFT as a function of nanoparticle concentration at pH 7 is also shown graphically in Figure 3. The change in IFT of water/crude oil from 22.4 to 12 mN/m in the presence of 1 wt% 5 nm PEG modified nanoparticles in dispersion indicates adsorption of nanoparticles at the interface. The concentration of nanoparticles at the interface was calculated using Equation 1. The concentration of PEG in aqueous solution and PEG attached to silica nanoparticles partitioned to the interface was quantitatively determined by using thermodynamic theory of partitioning (Gibbs equation):

$$\frac{d\gamma}{dC_2} = -\Gamma_2 \frac{RT}{C_2}$$

(1)

where R is the universal gas constant, T the temperature, C_2 bulk concentration, γ interfacial tension and Γ_2 is the concentration at interface.

The adsorption isotherms are given in Figure 4. The effect of pH was also studied. The change in IFT as a function of nanoparticle concentration at pH 9 is shown in Figure 3. In the absence of nanoparticles, the IFT of crude oil/water at this pH was 6.1 mN/m. As nanoparticle concentration increased, IFT decreased further. However, it reached a plateau around 3 mN/m for concentrations > 10 wt%. A similar behavior was observed with nanoparticle

dispersions at pH 7. This observation can also be made with the plateau in adsorbed concentration in Figure 4.
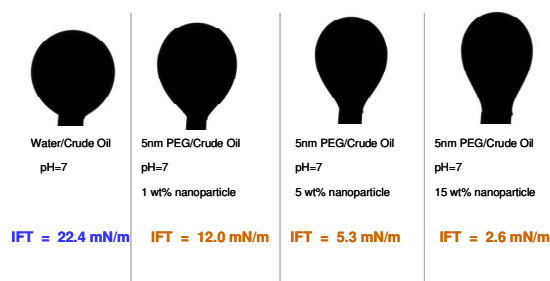

Figure 2– Interfacial tension (IFT) measurements for nanoparticle dispersions/crude oil. The aqueous nanoparticle dispersions are at pH 7 and there is no background electrolyte.
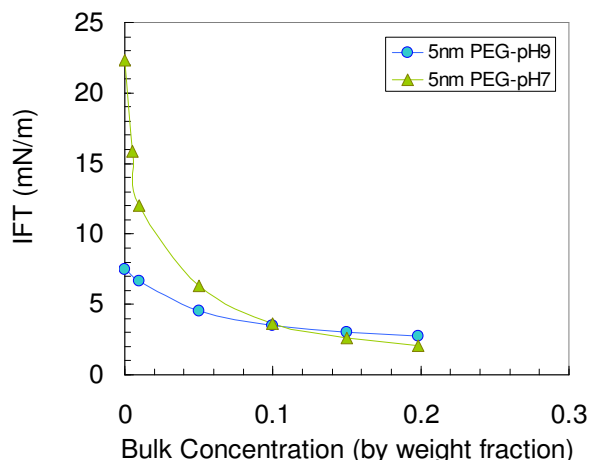

Figure 3– The change in IFT of crude oil/water as a function of 5 nm PEG modified nanoparticles at pH 7 and 9.
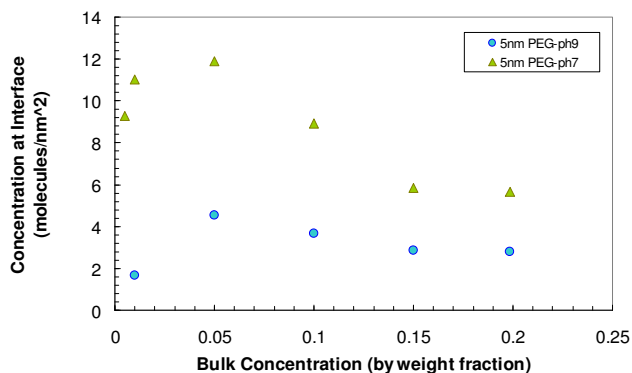

Figure 4– The adsorption of nanoparticles at the crude oil/water interface. The concentration of 5 nm PEG

modified silica nanoparticles at the interface as a function of bulk concentration at pH 7 and 9.

From batch experiments of IFT, we advacned to dynamic measurements. Glass bead pack with permeability of 7 D as described above was saturated with crude oil and then flooded with water at pH 7 without any background electrolyte until residual oil saturation was reached. A tracer test of aqueous solution of 0.05 wt% NaCl at pH 7 was injected to determine the residual oil saturation. Then the glass bead pack was flooded with DI water for several pore volumes until the conductivity of effluent reaches that of DI water. The injection of 5 wt% 5nm PEG modified nanoparticles started immediately after the water injection. The flow rates of water, tracer and nanoparticle dispersion are kept the same at 160 ml/hr to eliminate the effect of mobilization of oil because of hydrodynamic force. The effluent was collected to determine the concentration of tracer and nanoparticle as a function of pore volume injected. A picture of the glass bead pack is shown in Figure 5 at the end of water flood. The dark spots are residual oil.

We did not observe any improved oil recovery during nanoparticle injection. The normalized concentration (Equation 2) is plotted as a function of cumulative injection in terms of pore volume (PV) in Figure 6.

$$C_{norm} = \frac{C - C_{res}}{C_{inj} - C_{res}} \qquad (2)$$

where C is the concentration of the tracer or nanoparticle in the effluent, C_{res} the concentration in the resident fluid and C_{inj} is the concentration in the injected fluid.

In the absence of oil, both the tracer and nanoparticle dispersion show same profile as discussed elsewhere [7]. This result is consistent with our previous findings, showing that the nanoparticles do not adsorb on to glass (silicate) and act as a conservative tracer [1]. The concentration profile of the tracer in the presence of oil shows that the residual oil saturation was 12 % which agrees well with the calculations from the material balance of injected and produced oil. In the presence of oil, PEG modified nanoparticles adsorb at the water/residual oil interface as shown with IFT measurements. Hence, the shape of the normalized concentration curve for nanoparticles is different from that in the absence of oil. Although nanoparticles are retained at the oil/water interface, decreasing the IFT from 22.4 mN/m to 7 mN/m, we did not observe any oil recovery under the conditions as described above. Note that to displace residual oil, a critical value of capillary number must be reached;

$N_{Ca}^* = \dfrac{u\mu_w}{\gamma_{ow}} > 10^{-5}$, where u is the Darcy velocity; μ_w is the viscosity of aqueous phase; and γ_{ow} is the IFT of water or nanoparticle dispersion/oil. For our experiments, N_{Ca}^* is

4×10^{-6} for water and 10^{-5} for 5wt% 5nm PEG modified nanoparticle dispersions at pH 7 without any background electrolyte concentration. Therefore our observation of indiscernible oil recovery is supported by theory.

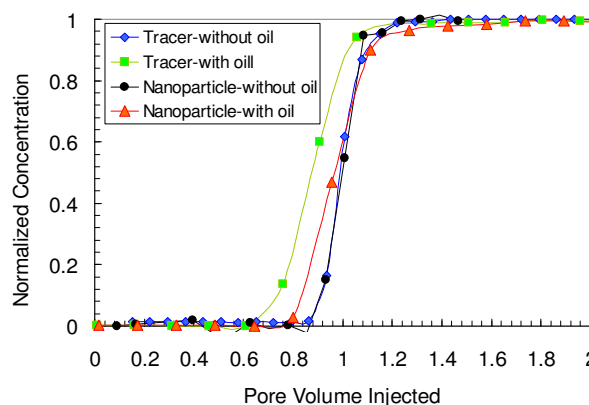Figure 5–Picture of the glass bead pack at residual oil saturation.

Figure 6–The effect of residual oil on the retention of PEG coated silica nanoparticles in porous media composed of glass beads.

4   CONCLUSIONS

Unmodified nanoparticles do not change the IFT of crude oil/water interface. However, the presence of PEG modified nanoparticles in solution lower the IFT. The interaction between the surface modified nanoparticles and the natural soap was very obvious. In the absence of crude oil, the nanoparticles act as a conservative tracer with insignificant interaction with the glass beads. This result is in agreement with our previous work on the adsorption of silica nanoparticles on mineral surfaces [1]. However, at the residual oil saturation of 12%, PEG modified silica nanoparticles are retained at crude oil/water interface as shown by the concentration profile. These results are also in

agreement with IFT and contact angle measurements carried out in this study.

ACKNOWLEDGEMENTS

REFERENCES

[1] C.O. Metin, J.R. Baran Jr. and Q.P. Nguyen, "Adsorption of Surface Functionalized Silica Nanoparticles onto Mineral Surfaces and Decane/Water Interface," Petroleum Preprints Presented at the 242nd ACS National Meeting, 2011.

[2] Y. Lee, Z. Du, W. Lin and Y. Yang, "Monolayer Behavior of Silica Particles at Air/Water Interface: A Comparison Between Chemical and Physical Modifications of Surface," J. Colloid Interface Sci. 296 (1): 233-241, 2006.

[3] B.P. Binks and C.P. Whitby, "Nanoparticle Silica-Stabilised Oil-In-Water Emulsions: Improving Emulsion Stability," Colloids and Surfaces A 253 (1-3): 105-115, 2005.

[4] F. Bresme and M. Oettel, "Nanoparticles at Fluid Interfaces," J. Phys. Condens. Matter 19: 413101-1-413101-33, 2007.

[5] Rame-Hart, http://www.ramehart.com/

[6] DROPimage, http://folk.uio.no/fhansen/dropbroc.html

[7] C.O. Metin, R.T. Bonnecaze and Q.P. Nguyen, "The Viscosity of Silica Nanoparticle Dispersions in Permeable Media," SPE 157056 paper presented at SPE International Oilfield Nanotechnology Conference and Exhibition, Noordwijk, The Netherlands, 12–14 June 2012.