Fate and transport of nanohybrids in subsurface media for oil field applications

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ABSTRACT
Interfacially active carbon nanotube hybrids have potential to be used in reservoir development applications. Carbon nanotubes hybrids (CNT) can act as carriers for catalytic nanoparticles into regions far inside the reservoir; they have the ability to stabilize water/oil interface in emulsions or can be used as contrast agents or sensors. One of the main challenges for successful utilization of these nanoparticles is the difficulty associated with stabilizing their dispersions and propagating them through the wellbore rock or deep inside the reservoir in harsh reservoir conditions of salinity and temperature.

In this work, CNT were dispersed in high salinity brine using a combination of two polymers Gum Arabic (GA) and hydroxyethyl cellulose (HEC-10) and were propagated through porous media with minimum retention. It was found that GA is able to debundle the nanotubes into individual ones by adsorbing on the surface of nanotube while HEC-10 is thought to generate steric repulsion that keeps the tubes well dispersed and prevent them from agglomeration in the presence of high salt concentration. The combination of these two dispersing polymers was found crucial for successful propagation of nanohybrids through consolidated or unconsolidated porous media.

Stable CNT dispersions have been propagated with low retention through 6” Berea cores of permeabilities as low as 200 mD in 10% brine (8% NaCl and 2% CaCl2) and a temperature of 65°C. Carbon nanotube adsorption inside the core was found to be ranging between 0.02 and 0.04 mg per gram of dry core weight and the overall nanotubes cumulative recovery was more than 80% of the injected nanoparticles with a normalized CNT concentration approaching 97% of the injected concentration. Increased retention of nanohybrids in the presence of oil in an oil pretreated core in comparison to an oil-free core has been observed which suggests adsorption of nanohybrids to the oil/water interface inside the core.

The demonstration of the successful propagation of CNT through Berea cores is an important first step in the process of incorporating them into advancing reservoir characterization and/or enhanced oil recovery technologies.

INTRODUCTION
Nanoparticles have demonstrated ability to stabilize water/oil interface (Crossley, et al. 2010, Shen and Resasco 2009, Binks 2002). They can be used as carriers for catalytic particles and have potentials to be used as contrast agents or tracers (Drexler, et al. 2012, Kadhum, et al. 2013, Berlin, et al. 2011, Hwang, et al. 2012). Nanoparticles have the ability to stabilize foams that can be used in drilling floods and mobility control (Resasco, et al. 2013). The main challenge for using nanoparticles in reservoir applications is the difficulty associated with dispersing and propagating nanoparticles in high reservoir salinity and temperature (Baez, et al. 2012, Villamizar, et al. 2010).

Dispersions of CNT in DI water case were first achieved using Polyvinyl Pyrrolidone(PVP) or Gum Arabic(GA) (Kadhum, et al. 2013). However, the ability of PVP or GA to disperse and propagate nanohybrids is drastically lost by the presence of high ionic strength (high salinity) in the dispersion. In earlier work, we demonstrated the ability to stabilize dispersions of purified multiwalled nanotubes (P-MWNT) in conditions of high salinity up to 10% and temperature up to 80°C (Kadhum, et al. 2013). This has been done by using two nonionic commercially available polymers with strong interaction with the tubes. The first one (primary dispersant) is either PVP of 40kD molecular weight or GA and it is believed that either polymers provides electrostatic repulsion which help in de-bundle the tube aggregate upon dispersion by sonication (Smalley 2002, Bandyopadhyaya and al. 2002). The second one is HEC-10, a salt tolerant polymer and is thought to provide steric repulsion (Kadhum, et al. 2013). Stable P-MWNT dispersions generated using GA and HEC-10 have shown little to no adsorption onto Berea sand at conditions of high salinity and temperature. This was demonstrated
through a number of adsorption isotherms and propagation column experiments (Kadhum, et al. 2013). The results of that work showed the low retention of nanohybrids in crushed Berea sand packed columns. It was found that injecting few pore volumes of nanohybrids would saturate available adsorption sites onto the Berea sand resulting in subsequent injection of nanotubes to be propagated completely (Kadhum, et al. 2013).

In this work, coreflood experiments were conducted as a part of this work to demonstrate the applicability of utilizing such nanotube hybrids in future reservoir applications. P-MWNT was dispersed by sonication in a solution containing GA. HEC-10 was added later and the dispersion was sonicated again. The dispersion was then filtered using 1um filter paper to remove large aggregates that can be retained at porous rock entrance (column sand face). The dispersion was then injected through number of cores ranging from 200-460mD. More than 80% of injected particles propagated successfully through the core with increased retention of nanoparticles in the presence of oil inside the core due to the nanohybrids preferential adsorption at the oil/water interface. The method of dispersing the nanoparticles was found important for optimum dispersion stability and propagation.

Materials. The CNT nanohybrids are amphiphilic materials with tailored hydrophilic/hydrophobic balance. The starting material consisting of multiwalled carbon nanotubes was provided by SouthWest Nanotechnologies Inc. (SWeNT), Norman OK. Nanotube growth is controlled to the desired length (~ 1 micron) and number of walls (~ 10) by adjusting the synthesis conditions. The alumina support and metal catalysts used in the growth process are later dissolved by an acid attack leaving a purified P-MWCNT product with > 98% carbon content. To adjust the interfacial activity of the CNT nanohybrids, the hydrophilicity of these nanotubes is increased by oxidation creating hydrophilic carboxylic groups on the nanotube surface (Kadhum, et al. 2013).

DI Water was purified and deionized using three ion exchange units from Cole Parmer. Gum Arabic was provided by Acros Organics and hydroxyethyl cellulose (HEC-10) was provided by Dow Chemicals. Sodium chloride and calcium chloride were provided by Sigma Aldrich.

Procedures. Purified multi walled carbon nanotubes were dispersed in brine with GA at the desired concentrations (indicated later) by sonication with a 600 W, 20 KHz horn-sonicator. HEC-10 stock solution was prepared according to guidelines published elsewhere (Scheuerman 1983) and added to the dispersed solution of P-MWNT to set an HEC-10:GA ratio of 8:1. Subsequently, the solution is sonicated again and centrifuged for one hour at 2000 rpm to eliminate any non-dispersed large aggregates of P-MWNT that settle in the bottom of the centrifuge vial. The concentration of all suspensions was measured on an UV-Vis spectrometer and compared to calibration standards of known concentrations, as described elsewhere (Attal, Thiruvengadathan and Regev 2006). The salinity through all experiments was 10% by weight, keeping a constant Na:Ca ratio of 4:1 in all experiments.

Coreflood experiments of stable dispersions have been tested in a core flood test setup. The core flood experiments depicted in Figure 1 consists of a syringe pump filled with mineral oil connected to four pushing pistons which will be filled with injected fluids. A core holder can hold core up to 6” in length is situated inside a heating oven connected to a temperature controller. Three pressure transducers are connected to a computer to record pressure changes during experiment. The effluent stream of the core holder is connected to a sample collector. Samples from the effluent were collected and analyzed using UV-Vis and converted into concentrations using calibration curves.

Dispersion of P-MWNT was prepared in GA stock solution by sonication for two hours and then HEC-10 solution was added and the dispersion is sonicated again for another thirty minutes. The final dispersion is 100ppm of P-MWNT, 200ppm of GA and 1600ppm of HEC-10. The salinity is 10% by weight consisting of 8% sodium chloride and 2% calcium chloride. The solution was centrifuged for 1 hour at 2000rpm and filtered using 1um glass microfiber filter papers (grade B) obtained from the Lab Depot Inc.

1 Experimental

First set of experiments have been done using two cores of Berea with measured permeabilities of 460 and 253mD. The breakthrough of a 100ppm dispersion of nanotubes is shown in Figure 2. The core tested were both 1” in diameter. Five pore volumes of dispersion were injected at 50°C and 5 pore volumes of brine post flush. In this figure it was observed that the concentration of nanoparticles is approaching C/C₀ of 1 after 5 pore volumes of dispersion injection with the 460mD core. The core with the lower permeability did not reach a plateau of C/C₀ after 5 pore volumes. This means that higher concentration approaching injected one could be achieved if dispersion is continued to be injected.

The total cumulative recovery was 98% for the 460mD core and 79% for the 253mD core. The transport of particles showed little to no retention at the sand face and we were able to propagate the dispersion successfully. Figure 3 shows photos of the 253 and 460mD cores. The 253mD core has been pre-flush with 1600ppm of HEC-10 polymer. The entrapments of particles at the sand face were very low as will be demonstrated later. Despite the fact that we got 79% recovery for this core, it is
anticipated that some of the particles were trapped at the sand face due to size exclusion due to the polymer pre-flush. The run with the 460mD core was done with sonicated polymer pre-flush and that eliminated greatly particle retention at the sand face. It is noteworthy to mention that all later runs including the experiments run by Stim-Lab ones were done without polymer pre-flush and demonstrated outstanding propagation. These previous results were encouraging to test the propagation through a standard core testing facility which was done in collaboration with Stim Lab in Duncan, Oklahoma.

1.1 Verification of Coreflooding (Standardized Testing)
Core flooding experiments of dispersed P-MWNT through core samples have been repeated in collaboration with Stim Lab; an affiliate of Core Laboratories. Two tests have been run using a dispersion prepared at our labs at the University of Oklahoma. The dispersion was prepared in the same way mentioned earlier. All solutions were in 10% brine with sodium chloride to calcium chloride ratio of 4:1. Table 1 list all details for both runs at Stim Lab and physical properties of the cores used. The two cores were pre-flushed with 10% brine prior to the test. The first core was run with no oil present. The brine flow rate was ramped up to 40 mL/min to remove loose clay particles from the core pores. The flow rate was then slowed down to 2ml/min and kept for a while until pressure stabilizes. 8 pore volumes of 100ppm P-MWNT dispersion were injected followed by 4 pore volume of brine post-flush. The second run was slightly different. It was done by injecting ¼ pore volume of Iso-Par L oil, a standard oil, and then the flow rate of brine was ramped up to 40ml/min collecting any oil coming out of the column and then settling the flow rate of brine down to 2ml/min and letting the pressure stabilize prior to dispersion injection. The oil saturation (Sor) prior to dispersion injection was found to be 0.21. Figure 3 shows concentration and cumulative recovery of both experiments.

<table>
<thead>
<tr>
<th>Table 1 Stim Lab tests details.</th>
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<tr>
<td>Permeability klinkenberg, mD</td>
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<tr>
<td>Temperature, oC</td>
</tr>
<tr>
<td>Salinity, %</td>
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<tr>
<td>Core length, inch</td>
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<tr>
<td>Core diameter, inch</td>
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<tr>
<td>Flow rate, ml/min</td>
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<tr>
<td>Berea 400 core porosity, %</td>
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Propagation data shows faster breakthrough for the case where oil is present due to the less pore volume. This is because of the fraction of the pore volume taken up by the oil. Table 2 list maximum concentrations attainable for both tests, overall cumulative recovery and amount adsorbed per gram of dry core.

<table>
<thead>
<tr>
<th>Table 2 Core-Lab run propagation data.</th>
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<tr>
<td>Core</td>
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<tr>
<td>------</td>
</tr>
<tr>
<td>Max. C/Co</td>
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<tr>
<td>Cum. Recovery, %</td>
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<tr>
<td>Adsorption, mg/gcore</td>
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By inspecting adsorption values reported in Table 2 it is obvious that there is significant retention of particles in the second core where oil is present. The nanoparticles have higher adsorption in that case indicating that particles got retained at the oil/water interface due to the nanotube hybrids interfacial activity. It is important to mention from inspecting C/Co that the concentration never reached a plateau in all cases which signifies the possibility of saturating available adsorption sites allowing for the possibility of further injections to propagate completely without retention. Figure 4 shows the sand face for both cores with small sparse patches of particles deposited at the core entrances.

Since the core with oil retained 5% more of the total particles or 33% more than the oil-free core, it is expected that the difference is due to the adsorption of nanoparticles particles at the oil/water interface. This means that the nanoparticles can be used for the detection of oil phase presence so it can act as contrast agents. Another core flood experiment with higher concentration was also conducted and it came in agreement with our previous result as will be demonstrated later.

The pressure drop for the two tests was recorded as well and is shown in Figure 5. The shaded area corresponds to dispersion injection. In this Figure we observed in the case of no oil, the pressure drop is not significant (≈3psi). This is mainly because of viscosity change since HEC-10 contributes towards viscosity (Hodge 1998). In the presence of oil, less pore volume is available because of the oil phase so it contributes to the rise in pressure drop. The less accessible pore volume resulted also in faster breakthrough of particles as shown in Figure 3.

1.2 High Concentration Coreflooding Experiment
Experiment was conducted using the same setup described earlier in our labs. The nanoparticle concentration was twice as much as the earlier experiments and the dispersion was prepared the same way mentioned earlier. In this case the dispersion was filtered twice using the 1 micron filter paper. The core tested was 200mD with 1” in diameter, 2” length. The dispersion flow rate was 1 mL/min. Brine was allowed to...
flow at 1 mL/min and once the pressure stabilized, 8 pore volumes of dispersion were injected followed by 4 pore volumes of brine post flush. The temperature was kept at 65.5°C. The concentration and cumulative recovery for this run is shown in Figure 6.

Figure 6 shows the slightly higher recovery overall of the 2” high concentration core in comparison with the 6” core ran by Stim Lab, these is mainly is expected because of twice filtered dispersion. The total cumulative recovery for this 2” run was 88.5% in comparison to 85% for the 6” core. The adsorption was 0.02 mg/gcore for the 2” core in comparison to 0.03mg/gcore for the 6” core. The losses of particles are quite low in comparison to typical surfactants as have been highlighted in our earlier work (Kadhum, et al. 2013).

CONCLUSIONS
Coreflood runs conducted in our labs at the University of Oklahoma were in good agreement with the standardized runs at Stim-Lab, Duncan, OK. Successful propagation of nanohybrids through cores of 200mD permeability and 6” length were achieved. The particle recoveries through all core runs were greater than 80% and concentration reaching as high as 97% of the injected concentration. Adsorption values were equal or less than 0.03 mg/gcore. The increase in P-MWNT adsorption was observed in the presence of oil phase inside the porous media suggests adsorption of P-MWNT at the water/oil interface. Successful propagation and interfacial activity of P-MWNT can be utilized towards the use of nanohybrids in delivery of catalytic particles, contrast agents or wettability modifiers.

ACKNOWLEDGEMENT
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REFERENCES
Figure 1 Coreflooding test unit.

Figure 2 Normalized concentration (C/Co) [top] and cumulative recovery of particles [bottom].

Figure 3 Photo of core plug face after propagation of MWNT through a) 460mD [top] b) 253mD [bottom].

Figure 3 Normalized concentration of particles (C/Co) [Top] and nanohybrids cumulative recovery [bottom] in 200mD cores.
Figure 4 Core entrance photos for both core runs with and without oil.

Figure 5 Pressure drop for Stim-Lab runs using 200mD cores.

Figure 6 Core flood using 200ppm P-MWNT dispersion injection (triangles) in comparison to 100ppm run by stim lab(circles).