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ENHANCING THE EFFECTIVENESS OF CARBON DIOXIDE
FLOODING BY MANAGING ASPHALTENE PRECIPITATION

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Managing Asphaltene Precipitation

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TABLE OF CONTENTS

	<u>PAGE</u>
Objectives	1
Summary of Work Done	1
Asphaltene Aggregation or Self Association	1
Effect of gravity on the displacement in the 6-component system	4
References	6
Figures 1-11	7-15

Objectives

Objectives of this project are to understand asphaltene precipitation in general and carbon dioxide induced precipitation in particular. To this effect, thermodynamic and kinetic experiments with the Rangely crude oil were conducted and thermodynamic and reservoir models were developed.

Summary of Work Done

The onset of asphaltene precipitation was measured with Near-IR spectroscopy by the titration method. Critical Micelle Concentrations (CMC) values of Rangely field asphaltenes in toluene, trichloroethane and tetrahydrofuran were determined to be 2.92, 3.69 and 4.88 g/L respectively. It was found that CMC values increased with increasing solvent solubility parameters. The CMC for C7asphaltenes extracted from the Rangely crude oil was 2.99 g/L. The Rangely crude oil CMC was measured at 3.10 g/L. These results show that for systems comprising of Rangely oil and its asphaltenes, self association or aggregation is possible at concentrations at or above 3 g/L

One and two dimensional simulations with a 6component mixture representing the Rangely crude were completed.

Asphaltene Aggregation or Self Association

Onset is defined as the minimum amount of precipitant necessary to induce the precipitation of solids, believed to be asphaltenes. A number of methods have been developed to measure the onset of precipitation or flocculation of asphaltenes. Precipitation onset data have been reported with conductivity, reflective index and viscosity measurements.

Methods of measuring CMC in oils/mixtures (other than the NIR method used in this study) are by using calorimeter, surface tension measurement, interfacial tension measurement, Vapor Pressure Osmometry and SAXS (small angle xray scattering).

It is well known that the asphaltene in oil phase is not the same as the solution of asphaltenes in pure solvents. Even though the CMC phenomena of asphaltenes have been investigated in oil and polar solvents, there is still much debate about the roles of resins and aromatics in the oil phase. Andersen et al. (1991) reported that the resin did not participate in micelle formation.

Cimino and coworkers (1995) presented onset data for the asphaltene-toluene-pentane mixtures. The range of concentrations was ca. 2.9~17 g/L, and this was a linear relationship between pentane and toluene. Mohamed and coworkers (1999) showed breaks in interfacial tension data and viscosity measurements. They suggested the occurrence of CMC in asphaltene-solvent systems. Yudin et al. (1998) discuss diffusion limited aggregation and reaction limited aggregation of asphaltenes from toluene asphaltene mixtures on addition of heptane. They found that at low initial concentrations of asphaltenes in toluene (1 g/L), the aggregation was controlled by diffusion, while, at concentrations of about 10 g/L, the aggregation was controlled by interaction between particles ("reaction").

The idea is that the asphaltenes aggregate differently according to concentration. At lower concentrations, asphaltenes are dispersed monomerically, while asphaltenes self aggregate at higher concentrations. Thus, the onset behavior is expected to be different in both cases.

Experiments Performed

Field-asphaltenes in this study were obtained from the Rangely field in western Colorado. Toluene and n-heptane were HPLC grade. Near-IR spectra were collected over the 1200 to 2400nm spectral region with Quantum-1200 (from LT Industries, Inc.) spectrometer consisting of a fiber optic detector. The spectra were collected through a probe equipped with a sapphire lens. The path length was 6 mm. Scans were collected every minute.

A fixed amount of ground field-asphaltenes was dissolved in toluene, trichloroethane(TCE) and tetrahydrofuran(THF) separately. Different asphaltene-solvent mixtures in the concentration range of 1 to 15 g/L were prepared. Heptane insoluble asphaltenes (C7-asphaltene) were prepared from the Rangely crude oil. The crude oil was mixed with heptane in the ratio of 1 to 10. After 24 hour stirring, the asphaltene was filtered with a 2.7 μ m pore size filter. The filtered asphaltene was dried until the weight was constant. Original amount of asphaltene, thus measured was 1.7 wt.%. Mixtures of n-heptane asphaltenes and solvents were also prepared in a manner identical to the procedure described for field asphaltenes.

Titration by heptane was carried out with 40mL of mixture. Schematic diagram of the experimental system is shown in Figure 1. The flow rate of heptane was controlled to 1 mL/min by peristaltic pump. The NearIR spectra were obtained with the probe directly placed inside the mixture. The error in measurement was 0.025 mL-heptane / mL-mixture.

Results and Discussion

Figure 2 shows spectra for three field-asphaltene/toluene/heptane mixtures; one of the spectrums is without addition of any heptane and the asphaltene concentration in toluene at 1 g/L, while the other two spectra are for the additions of 43 mL and 150 ML heptane to this mixture respectively. The absorbance at 1600nm for the mixture (Figure 2) shows relatively low background value. Typical titration induced NearIR absorbance at a wavelength of 1600nm is shown in Figure 3. The data is from heptane titration with the field-asphaltene/toluene mixture (1g/L). The initial decrease by precipitant dilution was followed the minimum value, which is identified as the onset of asphaltene precipitation. The absorbance continues to increase as the particles grow and agglomerate. As the particles they tend to settle or precipitate, a slight decrease in absorbance is noted. The absorbance changes at various concentrations (1~15g/L) of field-asphaltene/toluene mixtures were measured (Figure 4). The minima corresponding to flocculation onset are

shown with symbols on the figure. It is noted that as the asphaltene concentration increases, the absorbance values increase.

Figure 5 shows the precipitation onsets at various concentrations of field-asphaltenes in solvents – toluene, TCE and THF, respectively. Two distinct regions are noted; the initial period, where the onset decreases sharply followed by a notable change in slope after which the onset changes more gradually. This trend is observed for all the three solvents. Onset data where the slope change occurs is presented in Table 1. The break points for each solvent were 2.93 g/L (toluene), 3.69 g/L (TCE) and 4.88 g/L (THF). It is observed that the value of the onset at the break point increased as the solubility parameter increased. The solubility of solids in solvents can be generally understood in terms of the difference of solubility parameters between the solid and solvents.

In Figure 6, precipitation onset points for C7-asphaltene/toluene mixtures are plotted as function of asphaltene concentration. The onset points, in general, shifted upward, while the break point occurred at 2.99 g/L. In comparison to the field asphaltenes, the C7-asphaltenes were more stable, possibly due to their lighter nature.

The same data for Rangely oil is presented in Figure 7. Here the onsets are once again, shifted higher and the break point occurs at 3.1 g/L. Thus, the oil appears to be the best solvent for asphaltenes, where the asphaltenes are most stable.

Effect of gravity on the displacement in the 6-component system

Six Components, 1-D Simulations

A simulator with 20 x 1 x 1 Cartesian grid was developed. The dimensions of the grid blocks in the I direction $DI = 3.0$ feet, the dimensions of the grid blocks in the J direction $DJ = 0.025$ feet, and the dimensions of the grid blocks in the K direction $DK = 0.025$ feet. The porosity is constant throughout the domain, and is equal to 0.3. The components used were CO₂, normal butane, pseudo-hydrocarbon component of carbon number 10 (termed

(FC 10), FC16, FC30 and FC45. The initial compositions were 0.0,0.1,0.3,0.3,0.2 and 0.1 respectively. Pressure was maintained constant along the length of the reservoir bed. Straight-line relative permeabilities were used in the simulator. Pure CO₂ was injected at various pressures into the reservoir. The compositional paths at various pressures, 1500psia, 1900psia, 2500psia, and 3000psia were studied. In Figure 8 oil-phase compositions of different components (normalized with respect to their original concentrations) are plotted versus pore volumes injected. The implications of increasing pressure in 1-D displacements are clear. As pressure increases, heavier components are also recovered. For example, at lower pressures (1500, 1900 psia), most of the light components are recovered by the time 2-4 PV are injected, while the heavier components (FC30, FC45) are still in the oil phase. At higher pressures, these components are also recovered.

Six Components, 2-D Simulations

A simulator with 20 x 1 x 5 Cartesian grid was developed. The dimensions of the grid blocks in the I direction DI = 100.0 feet, the dimensions of the grid blocks in the J direction DJ = 1.0 foot, and the dimensions of the grid blocks in the K direction DK = 30 feet. All the other parameters were the same as the ones used in one-dimensional simulations. The compositional profiles in the middle block (10) were plotted as a function of pore volumes injected in the top (top two layers), middle (the middle layer) and the bottom (the bottom two layers) (Figures 9-11).

The recovery is quicker in upper layers due to the CO₂ override. Some of the oil from the upper layers drains into the lower layers. Some of the heavy components are not recovered from the lower layers despite injection of several pore volumes. Thus, the compositional variations in the different layers are different and this may lead to a heterogeneous precipitation environment, even in geologically homogeneous reservoirs. The simulation studies being undertaken now will examine if Water Alternating Gas (WAG) injection being carried out in Rangely corrects this compositional heterogeneity.

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Table 1. Critical Micelle Concentrations of asphaltenes.

	Toluene	TCE	THF
CMC	2.93	3.69	4.88

- C7-asphaltene/toluene : 2.99

- Oil/toluene : 3.10

Figure 1. Schematic diagram of the experimental system used.

Figure 2: Near-IR spectra of an asphaltene-toluene mixture (1g/L) and of mixtures with additions of heptane (43mL, 150mL) to the mixture.

Figure 3: Typical Near-IR absorbance curves at a wavelength of 1600nm by heptane titration of 1.0 g/L asphaltene-toluene mixture.

Figure 4: Near-IR absorbance curves at a wavelength of 1600nm by heptane titrations of different field-asphaltenes/toluene mixtures.

Figure 5. Onset changes as a functions of asphaltene (field) concentration in solvents, toluene, TCE and THF; change in slope possibly signifies Critical Micelle Concentration (CMC).

Figure 6. Onset changes as a functions of asphaltene (heptane derived) concentration in solvent, toluene.

Figure 7. Onset changes as a functions of asphaltene (in oil) concentration in a solvent comprised of oil and toluene. (Here, the amount of solvent was the amount of deasphalted oil and toluene)

Figure 8: Compositional variations of different components (in comparison to their original concentrations) at increasing pressures. Compositions in the oil phase for the tenth (10) block are shown as functions of pore volumes injected.

Figure 9: Compositional variations of different components (in comparison to their original concentrations) at different locations in the reservoir. Compositions in the oil phase for the tenth (10) block are shown as functions of pore volumes injected. The pressure in all the plots is 1900 psi.

Figure 10: Compositional variations of different components (in comparison to their original concentrations) at different locations in the reservoir. Compositions in the oil phase for the tenth (10) block are shown as functions of pore volumes injected. The pressure in all the plots is 2500 psi.

Figure 11: Compositional variations of different components (in comparison to their original concentrations) at different locations in the reservoir. Compositions in the oil phase for the tenth (10) block are shown as functions of pore volumes injected. The pressure in all the plots is 3000 psi.