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Effects of asphaltenes and organic acids on crude oil-brine interfacial visco-elasticity and oil recovery in low-salinity waterflooding

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ABSTRACT

Smart-water flooding has become increasingly more important as Enhanced-Oil Recovery technology in recent years. However, the observed incremental recovery varies significantly from case to case, even when the reservoir rock lithology, and water and oil characteristics are similar. In our earlier research, we proposed that a favorable crude-oil brine film visco-elasticity response reduces oil trapping during waterflooding and consequently increases oil recovery. We also advanced the idea that the film response depends upon a combination of crude oil and water characteristics. The purpose of this research is to show that the crude oil asphaltenic and acid fractions have a noticeable effect on interfacial rheology, while benefiting oil recovery in coreflooding experiments. In this work, ^{1}H NMR (Proton Nuclear Magnetic Resonance) was used to track changes in organic acid concentration in aqueous phase-crude oil partitioning experiments. Interfacial visco-elasticity measurements were conducted on several brine-crude oil sets as well as crude oil/brine volumetric ratios. On the other hand, emulsion stability was examined through low-field NMR drop-size time courses to evaluate coalescence. Finally, carefully selected coreflooding experiments were run to measure oil recovery and pressure drop as functions of time. The crude oils analyzed exhibit differences in asphaltene content and bulk acid concentration partitioned into the aqueous phase. These differences contribute dissimilarly to interfacial rheological behavior. In all cases, interfacial visco-elasticity increases the greater the asphaltene concentration and decreases at higher acid concentration for a given brine. The elastic modulus reaches a plateau value after a time specific to each brine-crude oil system. The effects of acids and asphaltenes appear to depend on the volumetric crude oil-to-brine ratio. Coreflooding recovery factor results show a positive correlation with dynamic interfacial properties, though not a straightforward one. Emulsions stability turns out to also be a complex function of the aforementioned interfacial properties and does not directly correlate to oil recovery. Our findings reveal that the nature of the fluids in the oil reservoir makes a significant difference in terms of fluid-fluid interactions. These may affect multiphase flow in porous media and consequently the final oil recovery after waterflooding. When this is better understood, a better design strategy to achieve optimal brine modification can be proposed to increase the oil recovery.

1. Introduction

The observation that changes in injection brine composition affect oil recovery was first recognized by Morrow et al. in the early 90s [1–3]. Subsequently, it was published that brine composition, and moreover the specifics of crude oil/brine/brine rock systems, affect oil recovery [4]. As a result of these findings, low-salinity waterflooding gained popularity, since Tang et al. [5] published encouraging recovery results using Berea sandstone cores. They showed that brine and oil compositions as well as aging temperature affected wettability and oil recovery. Changes in wettability toward water wetness occurred in experiments where low-salinity brine was used as connate brine or as injection fluid. These results were confirmed by in imbibition experiments at high temperature [6]. Initial hypotheses to explain enhanced-oil recovery (EOR) results in low-salinity brine injection included the presence of mobile fines, the existence of initial water saturation and exposure to crude oil to create a mixed-wet condition [7]. Since the seminal published work, wettability alteration upon injection of low-salinity brine in sandstone cores has been considered a

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primary EOR mechanism. British Petroleum (BP) registered LoSal technology after extensive research [8–10]. They showed that this process increases oil recovery compared to conventional waterflooding. In addition, significant research work has been pursued to find out effects of water chemistry on waterflooding recovery. Despite progress, a controversy on what the dominant low-salinity waterflooding recovery mechanisms has lingered for several years. Mechanisms claimed to explain low-salinity waterflooding recovery include primarily wettability alteration [11–15], interfacial tension (IFT) reduction, in situ emulsification [16,17] and fines migration [18,19,13].

Many studies on low-salinity have focused mainly on the significance of rock-fluid interactions, but often without a complete mechanistic description. Kafili et al. posed the questions as to whether wettability alteration is the main cause for low-salinity waterflooding recovery [20]. While their contact angle experiments on dolomite surface are used to link wettability alteration to enhanced recovery, nevertheless the evidence is somewhat indirect. A salient observation from special core analysis on core samples from the West Salym field in Siberia shows that the restored cores were quite water-wet prior to low-salinity waterflooding and yet additional recovery, while modest, was observed upon tertiary injection of low-salinity [21]. Zahid et al. indicate that the increase in oil recovery in the presence of sulfate ions in chalk cannot be satisfactorily explained through wettability alteration alone, since their cores were water-wet [22]. However, their evidence indicates that oil composition plays a role on oil recovery improvement. A decrease in crude oil viscosity in the presence of sulfate at high temperature, in addition to emulsion formation with the increase in sulfate ion concentration [23], has been observed. On the other hand, abundant evidence shows that water-in-oil emulsions can be stabilized in low-salinity brine by a buildup of a viscoelastic interface [24–26]. Fjelde et al. conducted careful experimentation to find out the impact of oil components, particularly acid/base ratios, on low-salinity waterflooding recovery. They linked adsorption of polar components on rock surfaces in sandstone that depended on both the composition of brine and/or crude oil [27].

The effect of fluid-fluid interactions on low-salinity has recently received attention. Some of our previous publications [28–30] show that a connection between recovery and increase in interfacial elasticity is likely to exist without a requirement of wettability alteration. Polar components in the crude oil are necessary for the overall recovery to improve [28,29]. In a similar sense, Mahzari and Sohrabi et al. propose a crucial fluid-fluid interaction during low-salinity water injection, namely the formation of a micro-dispersion at the interface as an important mechanism [31,32]. Meanwhile, Chakravarty et al. mention that aqueous solution can alter the micro forces at the oil-water interface forming oil-water emulsions, a process that depends on fines, acids and significantly the oil composition [33]. In previous publications [28,29], we demonstrated that the interfacial film between low-salinity brine and crude oils is more elastic than the film formed in the presence of high-salinity brine with the same ion types, and this correlates with the oil recovery during coreflooding experiments. In addition, when the aging time is not enough to build an elastic interface between the crude oil and the brine, or when the interface is destroyed intentionally, the oil recovery decreases. Chavez et al. report higher visco-elasticity and oil recovery at low-salinity concentration using microfluidic devices [34]. Moreover, reports show that breakup/snap-off and coalescence are the dominant processes responsible for phase connectivity and they take place concurrently during flooding, though one can be more dominant depending on oil saturation in the system [35,36].

We have found in our own work that organic acids can play a significant role in the buildup of viscoelastic brine-crude oil interfaces [25]. Exploration in the formation of water-in-oil micro-dispersions in low-salinity environments has been conducted, and a clear correlation between the asphaltene/resin ratio and the content of water-in-oil dispersion was found [31]. The accumulation of oil surface active component at the water-oil interface may cause an elastic interface [37]. This evidence on fluid-fluid interactions in low-salinity waterflooding indicates that additional mechanisms should be considered for this process.

Our earlier work focused on a particular crude oil from the State of Wyoming (TC). In this earlier work, we narrowed the brine composition down to sodium sulfate. We continued to use the same simple brine to allow comparisons. We are aware that different brines will induce different viscoelastic interfaces, but to reduce the size of the experimental matrix, only sodium sulfate was used in this work. To further investigate the role of polars and acids, we expanded our experiments to several crude oils containing different fractions of asphaltenes and organic acids. To scrutinize the effects of polars, crude oils were deasphalted and then mixed with portions of the original oil to manipulate the weight fraction of asphaltene in the blend. To show the effects of organic acids on interfacial visco-elasticity, a naphthenic acid blend was added to either the crude oil or the brine.

We show how the viscoelastic response of the brine-crude oil interface changes under shear rheology for different concentrations of the asphaltene fraction and organic acids. This has been shown to affect emulsion stability brine-crude oil systems [38–41]. Emulsion stability analysis through time-tracking of the droplet-size distribution suggests that coalescence enhancement under certain conditions that may influence oil recovery. Coreflooding experiments on Berea sandstone were conducted to evaluate the effect of low-salinity water flooding on the oil recovery response for different oil compositions Results show that addition of acids can increase oil recovery.

2. Materials

Eight different crude oils from either Wyoming or the Gulf of Mexico were used in this research. (MB, ZP, K, WG, GB, TC, RC, and LS). Basic properties for these oils are shown in Table 1.

Brines were prepared by dissolving analytical-grade Na_2SO_4 in deionized water (DW). This salt was selected to enable comparisons with results published previously. In this paper, 100% Na_2SO_4 is equivalent to an ionic strength of 0.6724 M, comparable to a connate water from a Wyoming reservoir. This brine was diluted by adding DW to obtain a brine at 1% Na_2SO_4, equivalent to an ionic strength 0.006724 M. Fresh solutions were prepared frequently to avoid bacterial or fungi growth.

Berea sandstone was used in the coreflooding experiments. The length, pore volume (PV), and porosity of each plug are listed in Table 2. The names indicate the crude oil used for each experiment.

A naphthenic acid (NA) blend from Sigma-Aldrich (70340-L; Lot & Filling Code: 1331432 31607282) was used to mimic the natural

Table 1
Crude oil properties at 25 °C.

Crude oil	Density (gr/cc)	Viscosity (cP)	C_5-asphaltene (wt%)	Refractive index
MB	0.98	18,929	23.7	
ZP	0.97	13,161	25.3	
K	0.96	4534	18.2	
WG	0.92	105	10.8	1.527
GB	0.91	94	10.2	1.517
TC	0.91	64	5.0	1.515
RC	0.86	13	1.1	1.482
LS	0.85	12	0.6	1.483